A THESIS

Topics in the Chemistry of Niobium and Tantalum Pentafluorides and other Higher Halides

Submitted to the University of Glasgow by J. C. Fuggle B.A. in part fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Science

Work presented in this thesis is the result of research carried out by the author, in the Chemistry Department of the University of Glasgow, between October 1968 and May 1971, except where specific reference is made to other publications.

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This thesis is dedicated to all those who have played a part in my education and in particular to my parents, whose share in the work involved was greatest, and probably most arduous.

"Ad apris ki bien conuist ahan"

Song of Roland (13th

"The converse is also true." - Ph.D student

GLASGOW 1971

I gratefully record my obligation to my supervisors, Professor D. W. A. Sharp and Dr. J. M. Winfield for their encouragement, advice, tolerance, and patience during the course of my work.

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Summary

Research presented in this thesis falls into four areas.

1) Vibrational spectra of pentafluorides.

2) Preparation and spectra of NbF_5 and TaF_5 complexed with Lewis bases.

3) Preparation and some properties of some Nb, and Ta (V) fluoride-halides and pseudohalides.

4) ^{93}Nb n.q.r. spectra of some compounds derived from NbF_5.

^{93}Nb n.q.r. spectra of NbF_5 and vibrational spectra of NbF_5 and TaF_5 are interpreted in terms of a very small deviation from C_{4v} symmetry in the tetrameric molecules of the solid state. I.R. spectra suggest that NbF_5, and TaF_5 are polymeric in the liquid state up to at least 150°C, but that the Lewis acid-base complexes formed by reaction of NbF_5, or TaF_5 with a series of oxygen, and nitrogen donor molecules contain no bridging fluorine atoms. Assignment of vibrational frequencies associated with the coordinated Lewis bases is almost complete. Vibrational and ^{93}Nb n.q.r. spectral data of 1:2 complexes of NbF_5, and TaF_5 prove neither the absence or presence of NbF_6^- or TaF_6^- anions.

Substitutions for F atoms in pentafluorides by NEt_2, Cl, Br, CN, NCS, NCO $(O)_{1/2}$ and $(NMe)_{1/2}$ groups using the reaction

of MF_5 or $MF_5.OEt_2$ (M= Nb,Ta) with Me_3Si reagents are reported. The products of substitution reactions were investigated by I.R., and Raman spectroscopy and x-ray powder photography. Evidence obtained suggests that the fluoride-dialkylamides are weaker Lewis acids than the parent pentafluorides and consist of fluorine-bridged polymers. Evidence obtained from other mixed halide materials is not sufficient to prove the absence of mixtures of compounds.

An investigation of the use of ^{93}Nb n.q.r. spectroscopy as an aid to study of some niobium compounds is reported. Resonances observed for NbF_5, $NbF_5.2Py$, $NbF_5.CH_2ClCN$, $NbF_5.Me_2O$, $NbF_5.XeF_2$, and $(NbF_5)_2\ XeF_2$ are assigned to the possible quadrupole transitions of the 9/2 ^{93}Nb spin system and some conclusions relevant to the structures of the compounds are presented.

Contents

Introduction

The history of investigations of halogens and halides is long and eventful. There can be little doubt that the corrosive, suffocating, greenish-yellow fumes of chlorine must have been known from the thirteenth century by those who made, and used, aqua regia.[1] The recognition of chlorine as an element was bound up with the evolution of the concept of "elements"[2,3] and with bromine, and iodine (established as elements in 1824[4] and 1813[5] respectively) it has been recognised as an element from the period at the beginning of the ninteenth century when "chemistry" may be said to have evolved from alchemy. Chlorine, bromine, and iodine may all be isolated by treatment of halides with oxidising agents, but no satisfactory 'chemical' method for isolation of fluorine has been found and only electrolytic methods are extensively used. Although the existence of an element "fluorine" was postulated in 1810[6] experimental difficulties, largely attributable to the extreme reactivity of fluorine, delayed its isolation until 1884.[7]

Many of the binary fluorides were known and recognised before the isolation of fluorine itself and by the end of the first third of the twentieth century, fluorides of most of the non-metallic, and main-group metallic elements, and a number of those of transition metals, were known. However, during, and after the Second World War a renewed interest in

fluorine chemistry was rewarded by the discovery of many new binary fluorides, culminating in the spectacular discovery of noble-gas fluorides in 1962[8,9].

It should not be inferred from the differences in the history of these halogens that either fluorine, or fluorides, are fundamentally different from the other halogens, or halides. The chemistry of the halides is more dependent on the metal, or non-metal, combined with halogen, and its oxidation state, than the halogen present (e.g. NbF_5 shows more similarity to $NbCl_5$ than PF_5). Fluorine atoms bond more strongly to other atoms and are more electronegative than other halogens and the F-F bond strength is weaker than the corresponding bond strength of the other halogens. This leads to higher reactivity of fluorine, with respect to other halogens, and a greater thermodynamic stability of fluorides with respect to other halides.

It is no coincidence that modern chemistry evolved from alchemy at about the same time that modern methods of scientific glassblowing were developed[10]

Use of silicate-based glasses has become almost fundamental in modern experimental chemistry. Fluorine, and many fluorides, react with silicate glasses, either alone, or in the presence of minute amounts of water which act as catalysts

i.e.

$$MF_x + H_2O \rightarrow MOF_{x-2} + 2HF$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Phosphate glasses are not attacked by fluorides, but are not suitable for glass blowing. Although many fluorides, e.g. WF_6,[11] do not react with dry glass very small amounts of water, or hydrogen fluoride, catalyse the reaction with glass which itself contains water, both in its surface layers and in the bulk, which can never be entirely removed by degassing.[12] Free hydrogen fluoride may also be produced by reaction of fluorides with hydrocarbon, and rubber-based greases.

Many higher halides are air, and/or moisture sensitive and dry-box techniques have been developed to handle air-sensitive materials. However no dry-boxes are perfect (some are worse than others) and whenever a moisture-sensitive fluoride is used in a dry-box it will inevitably pick up some moisture.

The above remarks suggest that experimental work with higher halides will always be done in conditions that are less than perfect, but that great care should be taken to ensure that water levels are acceptable. It is no insult to early workers in this field to state that some literature work is wrong, or unreliable, because of the possibilities of hydrolysis. Whilst the study of the chemistry of halides is very incomplete many trends in the chemistry of binary fluorides have begun to emerge.

All known hexafluorides, and heptafluorides are monomeric and volatile under vacuum, at room temperature. Pentafluorides

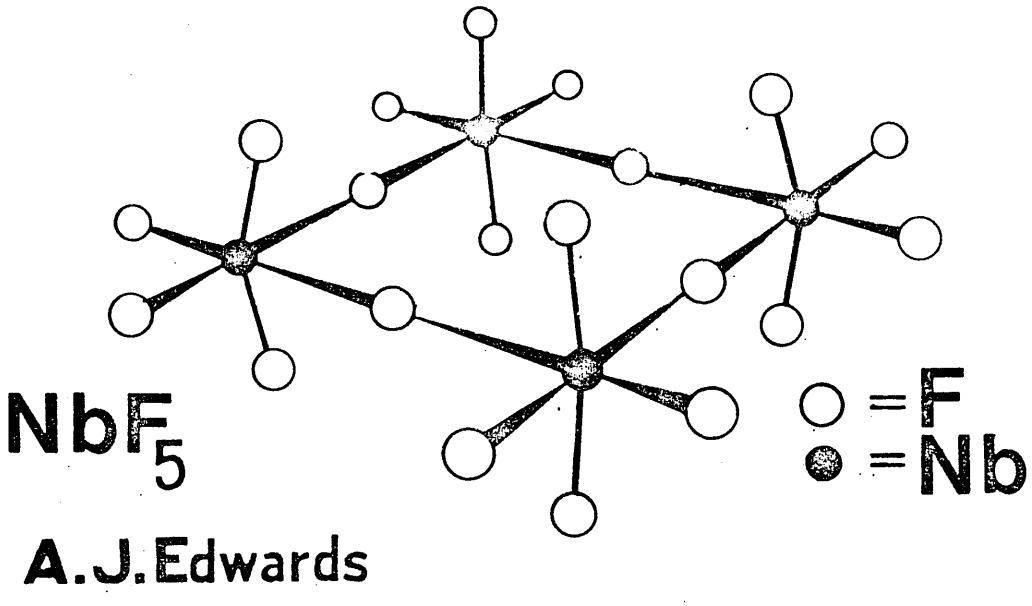

Fig I:1 Structure of NbF_5

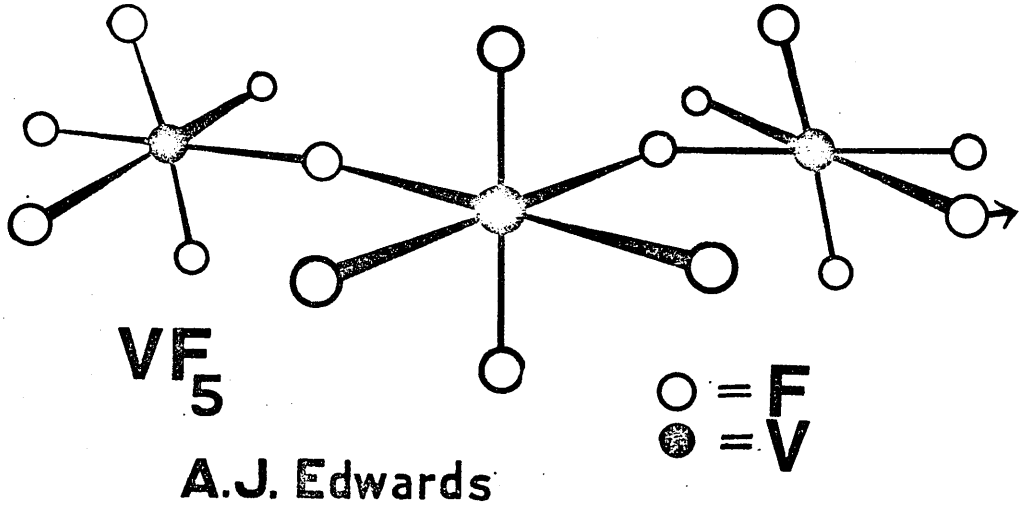

Fig I:2 Structure of VF_5

particularly of heavier elements, usually form fluorine bridged polymers in the solid state,[13,14] thus completing octahedral coordination about the central atom (see figures I: 1,2,). Transition metal tetra-fluorides and trifluorides are not, in general, well characterised, but usually have three-dimensional lattices, probably best regarded as an array of ions (e.g. ZrF_4,[15] NbF_4[16]).

These changes in structure are reflected in fluoride volatilities. The volatility of a series of metal fluorides increases with increasing valency of the metal. e.g. ReF_4 can be sublimed at 300°C [17] ReF_5, ReF_6 and ReF_7 have the boiling points 221 [19] (by extrapolation) 53.7, and 73.7°C [18] respectively.

There are not sufficient thermodynamic data available to be able to state absolutely what trends are present in transition metal-fluorine bond strengths. There is a regular decrease in the frequency of the a_{1g} stretching mode of transition metal hexafluorides as the metal is changed for metals further to the right of the periodic table. This is not proof that transition-metal-fluorine bond strengths are less for metals to the right of the periodic table, but the sequence fits in with the known chemical reactivity of hexafluorides. The relative reactivities of hexafluroides with NO, NOF, and Xe demonstrates this order of reactivity (Table I 1)[11]

Table I 1 Reaction Products of Transition Metal Hexafluorides.

Reactant	WF_6	ReF_6	OsF_6	IrF_6	PtF_6
NO	n.r.*	$NOReF_6$	$NOOsF_6$	$NOIrF_6$ $(NO)_2IrF_6$	$NOPtF_6$ $(NO)_2PtF_6$
NOF	$NOWF_7$ $(NO)_2WF_8$	$(NO)_2ReF_8$	$NOOsF_7$ $NOOsF_6$	$NOIrF_6$	$NOPtF_6$ $(NO)_2PtF_6$
Xe	n.r	n.r.	n.r.	n.r.	$Xe(PtF_6)_x$

The reactions summarised in table I1 are principally adduct or salt formations, or reduction of the transition metal. No systematic studies of halogen exchange reactions have been undertaken.

The transition metal fluorides become progressively more difficult to work with as their volatility decreases. Whilst volatile fluorides may be easily purified by distillation involatile fluorides may not. Further the involatile, lower fluorides of transition metals are insoluble in solvents with which they do not react, and this has so far proved an insurmountable barrier to purification of lower fluorides. The lower transition metal fluorides may be sensitive to oxygen, as well as water, and many of the reported lower fluorides are thought to contain large quantities of oxide-fluorides [11] e.g. NbF_5 [16,20] has lattice dimension very similar to NbO_2F [21], $NbO_{1.25}F_{1.75}$ and $NbO_{0.99}F_{2.25}$ [22] These experimental problems have probably been at least partially responsible for

the lack of studies of lower transition metal fluorides.

The research into the chemistry of NbF_5, and TaF_5, presented in this thesis was started with the intention of extending the knowledge of chemistry of transition metal fluorides in the direction of the lower fluorides, with a view of providing a possible basis for later studies of lower fluorides. NbF_5, and TaF_5 have physical and chemical, properties intermediate between those of MoF_6, or WF_6, and ZrF_4 or HfF_4[11]. NbF_5 and TaF_5 were chosen for study because their reactions are not complicated by oxidation, or disproportionation of the metal as Nb, and Ta have a maximum valency of five.

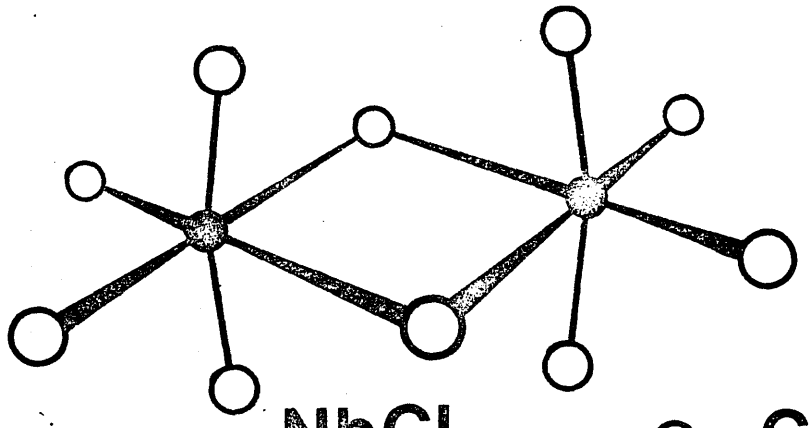

Figure I:3 Structure of $NbCl_5$

In nature the ores of niobium, and tantalum are normally associated and separation is extremely difficult because of the similarity of their chemical properties. That niobium and tantalum were two different elements was not, at first realised and true understanding of the identities of the elements may be dated to the work of Rose [23] between 1840 and 1845. However the reports of Berzelius in 1825 [24,25] suggest that he prepared nearly pure K_2TaF_7, and $TaCl_5$ and he may well have made TaF_5. Rose prepared $TaCl_5$, and K_2TaF_7 in 1856 and the vapour densities of $NbCl_5$ and $TaCl_5$ were first studied in 1866 [27,28]. After the first possible preparations by Berzelius other materials which might have been NbF_5, or TaF_5 were reported throughout the nineteenth century bu their characterisation was

not achieved until the early twentieth century.[29,30]

Niobium, and tantalum pentahalides are, with the possible exception of the iodides, polymeric with bridging halogen atoms[13,31] (fig I 1, I 3). Although seven, and even eight coordination is known for second, and third row transition metal compounds (see e.g. ref. 32,33), it is not common and in this respect these elements are intermediate between the first row metal[34] and actinide[35] halides, the former having a maximum coordination number of six, and the latter commonly being found with coordination number eight.[35] Fluorine is a good ligand and often brings out the highest coordination number of elements, e.g. IF_7,[36] ReF_7[37], K_2PaF_7[38]. In a study of niobium, and tantalum fluorides the possibility of higher coordination numbers should be considered.

This thesis is arranged in three chapters. The first deals mainly with vibrational spectra of the pentafluorides, and their Lewis acid-base complexes. The study of the complexes was started as a training exercise, but it rapidly became clear that a confirmatory study of much of the previous work was necessary. The second chapter deals with attempts to substitute other atoms, or groups of atoms, into NbF_5 and TaF_5 and to see if the Lewis acidity, and polymerisation properties of the products isolated were similar to the pentafluorides. Niobium and Tantalum nuclei have large quadrupole moments, which, together with the various exchange reactions undergone

in the compounds investigated make ^{19}F N.M.R. investigations of these materials very difficult. Chapter 3 deals with investigations into the use of n.q.r. spectrometry as an alternative probe of the nature of these compounds.

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CHAPTER I

Pentafluorides and their Complexes with Lewis Bases.

1:1 Introduction

G. N. Lewis [1] defined a basic substance as one "which has a lone pair of electrons which may be used to complete the stable group of another atom," and an acidic substance as one "which can employ a lone pair from another molecule in completing the stable group of its own atoms." Almost all pentafluorides act as Lewis acids under some circumstances (e.g. IF_5 [2], BiF_5 [3], PF_5 [4], RuF_5 [5], PaF_5 [6]. It should, however, be noted that not all of the pentafluorides act as Lewis acids in the original sense; Lewis thought of a stable group of electrons as a closed shell of valence electrons. It is perhaps better to define a Lewis acid as a molecule, with a high electron affinity, capable of forming a bond to a basic molecule by use of a lone pair of the base.

Amongst non-metal pentafluorides the strongest acidity is shown by those of group $\underline{V}$ B, whose acid strength increases along the series PF_5 AsF_5 SbF_5 There is, as yet, insufficient evidence to make a comparison between the Lewis acidity of metal and non-metal pentafluorides.

The reactivity of transition metal pentafluorides increases from left to right across the periodic table (e.g. RhF_5[7] oxidises CCl_4 to give ClF). It is probable that transition metal pentafluorides to the right of the periodic table would be reduced, or otherwise transformed, by all organic bases and studies of their Lewis acidity will be limited to acceptance of fluoride ions from inorganic fluorides (e.g. see refs 5,6). This chapter deals with the products of reaction between the less reactive transition metal pentafluorides, and ethers, thioethers, dialkyl selenides, dimethyl sulphoxide, amines, nitriles, and pyridines. With higher metal halides of reactivity intermediate between NbF_5 and RhF_5 (e.g. $MoCl_5$, TcF_5) all of these bases except nitriles and pyridines are known to break up, giving halogen replacement reactions.[17] Nitriles and pyridines tend to be oxidised by these halides (e.g. see refs. 31, 33, 35). By comparison with other metal pentahalides, niobium, tantalum and molybdenum pentafluorides are comparatively unreactive and give a large number of 1:1 and 1:2 acid:base complexes with organic donor molecules. Some of these complexes, along with new complexes prepared in these studies, are shown in Table 1:1:1

TABLE 1:1:1 ACID-BASE COMPLEXES OF NbF_5, TaF_5, MoF_5

NbF_5 complexes	ref	TaF_5 complexes	ref	MoF_5 complexes	ref
$NbF_5.OMe_2$	(9)	$TaF_5.OMe_2$	(9)	$MoF_5.OMe_2$	(16)
$NbF_5.OEt_2$	(9)	$TaF_5.OEt_2$	(9)		
$NbF_5.SMe_2$	(9)	$TaF_5.SMe_2$	(9)		
$NbF_5.SEt_2$	(9)	$TaF_5.SEt_2$	(9)		
$NbF_5.(C_4H_8S)_2$	(9)			$MoF_5.(CH_3CN)_2$	(16)
$NbF_5.CH_3CN$*	(12)	$TaF_5.CH_3CN$*	(13)	$MoF_5.CH_3CN$	New
$NbF_5.CH_2ClCN$	New	$TaF_5.CH_2ClCN$	New	$MoF_5.CH_2ClCN$	New
$NbF_5.CH_3CH_2CN$	New	$TaF_5.CH_3CH_2CN$	New		
$NbF_5.Me_2SO$	New	$TaF_5.Me_2SO$	New		
$NbF_5.(Me_2SO)_2$	(11)	$TaF_5.(Me_2SO)_2$	(11)		
$NbF_5.(Py)_2$	(10)	$TaF_5.(Py)_2$	(10)	$MoF_5.(Py)_2$	(16)
$NbF_5.(4Me\text{-}Py)_2$	New	$TaF_5.(4Me\text{-}Py)_2$	New		
$NbF_5.Me_2SO.Py$	New	$TaF_5.2Me\text{-}Py$	New		
$NbF_5.(NH_3)_2$	(15)			$MoF_5.NH_3$	(16)
$NbF_5.(NHMe_2)_2$	New	$TaF_5.(NHMe_2)_2$	New		
$NbF_5.(NHEt_2)_2$	(14)	$TaF_5.(NHEt_2)_2$	(14)		

*These complexes were reported in the literature after completion of this work.

The main aim of the work presented in this chapter was to investigate the vibrational spectra, and relationships between structure and spectra, of niobium, tantalum and molybdenum pentafluorides and their complexes with organic bases. It was also hoped that the vibrational spectra arising from bases coordinated to pentafluorides would give a possible basis for characterisation of mixed halides of niobium, tantalum, and molybdenum by adduct formation. Some space is given in section 1:6 to assignment of these bands.

To show the context in which the chemistry of this chapter should be seen it is necessary to mention some discrepancies between this and previous work.

Dimethyl sulphoxide reacts with many metal halides to break metal-halogen bonds and form metal-oxygen bonds. (18) The halo-alkyl sulphides produced are often unstable except when coordinated to a metal atom, and other products may be difficult to separate. Excess dimethyl sulphoxide is also capable of acting as a donor molecule to the oxyhalides formed e.g. (19)

$NbCl_5 + 3Me_2SO \rightarrow NbOCl_3.2Me_2SO + HCl + CH_3SCH_2Cl$

Replacement of the methyl groups in Me_2SO by increasingly electronegative groups (20) or coordination of a metal ion to the sulphur atom in Me_2SO (20) leads to an increase in $\nu S=O$. Bonding of a metal ion to the oxygen atom of dimethyl sulphoxide decreases the S-O bond order and $\nu S=O$ (21) This may be

used to differentiate between sulphur- and oxygen - bonded dimethyl sulphoxide complexes.

In this work, in the absence of a solvent, dimethyl sulphoxide did not react cleanly with NbF_5 or TaF_5. The reaction was very exothermic, and gaseous, and liquid by-products were formed. The reported dimethyl sulphoxide complexes of NbF_5 and TaF_5 were made without a solvent and no analytical data was given. (11) This, and other discrepancies between reported results, and those found here, suggest that $NbF_5.(Me_2SO)_2$ and $TaF_5.(Me_2SO)_2$ have not previously been obtained pure. Formulation of the compounds as ionic species (12) (MF_6^-, $MF_4L_4^+$) on the basis of conductivity in the molten complexes (11) is not valid because decomposition occurs on melting these complexes.

Aminolysis of higher transition metal halides by amines commonly occurs under mild conditions (22,23,24) Few aminolysis reactions of transition metal fluorides have been reported. However TiF_4 and dialkylamines undergo aminolysis (25) and recent attempts to produce the reported adduct $WF_6.(NHMe_2)_2$ (26) have failed because of aminolysis (27) It is likely that further investigation may show more fluorides to give aminolysis. The reported adduct $MoF_5.NH_3$ (16) was characterised only by metal analysis (which would be almost identical to that of $MoF_x(NH_2)_{5-x}.NH_3 [X=0-5]$) and gave a strong broad I.R. band at 550 cm^{-1} not found in other 1:1

adducts of MoF_5.

In this chapter only reactions of secondary amines are reported. Secondary amines are known to solvolyse two metal-chlorine bonds of niobium and tantalum pentachlorides [22,23]
e.g. $NbCl_5 + 5NHMe_2 \rightarrow NbCl_3.(NMe_2)_2.NHMe_2 + 2NH_2Me_2Cl$

The adducts $NbF_5.(NHEt_2)_2$, and $TaF_5.(NHEt_2)_2$ have been reported and are reinvestigated here. The formulation of the products of reaction of ethylamines with pentafluorides as 1:2 acid-base complexes was made partly on the basis of I.R. spectra of the products in ethanol and acetone solutions. Such spectra are of dubious value and bands of 3400, 1630 cm^{-1}, dismissed as being due to water absorbed during preparation, might be due to the presence of $NH_2Et_2^+$ ions formed by aminolysis $2NbF_5 + 4Et_2NH \rightarrow NbF_4.NEt_2.(Et_2NH)_2 + NbF_6^-Et_2NH_2^+$
No evidence was presented to prove the absence of amminolysis in the reactions performed.

It has been found that aminolysis of PF_5 [28] and $TiCl_4$ [29] by diethylamine occurs more readily than aminolysis by dimethylamine and this may be general.

The reaction
$NbX_5 + Et_2O \longrightarrow NbX_5.OEt_2 \longrightarrow NbOX_3 + 2EtX$ (X=Cl,Br) has been reported [30] but it is not clear how easily this reaction occurs. The literature report [30] that $NbCl_5.OEt_2$ loses ethyl chloride at room temperature does not agree with results presented here. $MoCl_5$ gives the adduct $MoCl_5.(OEt_2)_2$ with diethyl ether but in

the presence of a trace of moisture $MoOCl_3(OEt_2)_2$ is formed[31] [31] A trace of water in the reported $NbCl_5CEt_2$ may explain discrepancies between the reported work and that presented here.

$NbF_5.CEt_2$ may be vacuum distilled at 60°C [9] but WF_6 forms an oxyfluoride with diethyl ether at 0 °C [32] Reactions of this type with other transition metal halides have not been investigated.

The above information suggests that pentachlorides of niobium and tantalum undergo halogen replacement reactions more easily with organic bases than pentafluorides, but data on some reactions are still incomplete, and confused. No halide-replacement reaction have been observed for dialkyl sulphides and selenides, but few investigations have been made.

The ease of reductions of transition metal pentahalides by pyridine show the following trends :- $NbF_5 < NbCl_5 < NbBr_5 < NbI_5$, [10,33] $MoCl_5 > NbCl_5 > TaCl_5$ [31,33] The products of these reactions are usually a tetrahalide di-pyridine adduct and a mixture of bipyridyls. The ease of reduction of niobium pentachloride is a matter of some discussion in the literature [33,34] and some comments on this are made in section 1:6

Alkyl cyanides are weaker reducing agents than pyridine but do reduce molybdenum pentachloride. [35] Niobium and tantalum pentafluorides, [12,13] chlorides, [36] and

bromides [36] all give 1:1 adducts with nitriles. In addition a 1:2 adduct, $MoF_5(CH_3CN)_2$ has been characterised [16] and since work reported here was done, an adduct $NbF_5.(CH_3CN)_2$ was reported but no evidence was quoted.[37]

Since this work was started papers have been published on the 1:1 and 1:2 complexes of niobium and tantalum pentafluorides with ethers, sulphoxides, formamides, and pyridine stating that the 1:1 complexes have C_{4v} symmetry and the 1:2 complexes have a structure with MF_6^- and $MF_4L_4^+$ ions.[12,13] No evidence was given to support the C_{4v} structure for 1:1 complexes and the only evidence for ions in the 1:2 complexes was detection of MF_6^- ions by N.M.R. spectroscopy. The reported compounds were, in general, coloured whilst those prepared here were white or colourless. Nb(V) and Ta(V) are d^0 species and their compounds are expected to be white It is possible that reported colourations were due to impurities and that the MF_6^- ions detected by N.M.R. spectroscopy in solutions of 1:2 complexes were produced by hydrolysis.

The structure of niobium, tantalum, and molybdenum pentafluorides in the liquid state is discussed in section 1:5 Several studies of the vibrational spectra of niobium [38, 39, 40, 41] tantalum, [38, 40, 41, 42] and molybdenum [43, 44] pentafluorides have been made but these are not all in agreement, either with each other, or with this work, and they are discussed in section 1:4

1:2 Results

A large amount of vibrational spectral data has been accumulated in these studies. Despite the complexity of the molecules many I.R. and Raman bands can be assigned and it is convenient to divide the data into sections for discussion. Complete lists of observed I.R. and Raman spectra are presented in Appendix 3, along with results from x-ray powder photographs, and mass spectra of some of the compounds. Tables and figures of selected data are presented throughout the discussion section of this chapter.

It is believed that the products obtained from reactions with nitriles, ethers, dimethyl sulphoxide, pyridine, and 4 Methyl pyridine are pure and comprise adducts of 1:1 or 1:2 stiochiometry.

Details of the I.R. spectra of solid, and liquid niobium, and tantalum pentafluorides, Raman spectra of solid niobium and tantalum pentafluoride, and I.R. spectra of solid molybdenum pentafluoride are given in section 1:3.

1:3 Vibrational spectra and stereochemistry of metal pentafluorides

Since this work was started there have been five publications concerned with the vibrational spectra of solid and liquid pentafluorides of niobium, tantalum and molybdenum [38,40,41,43,44] The sets of experimental data are not all in agreement, either with each other, or with this work. Before discussing the implications of these spectra it seems desirable to discuss the variations in experimental results. Some recorded vibrational spectra of solid NbF_5, TaF_5, and MoF_5, and liquid NbF_5 and TaF_5 are given in tables 1:3:1 and 1:3:2. I. R. spectra of solid and liquid NbF_5 and TaF_5 are also shown in figures 1:3:1 a,b,c, and d.

The I.R. spectra of solid niobium, and tantalum, pentafluorides of Preiss et al, [38] are in reasonable agreement with the present work except in the region above 600 cm^{-1}, where differences in mulling technique, or reaction with the caesium bromide plates used by Preis may be important. Other differences are of little consequence and are attributed to different interpretation of band shapes and intensities.

The differences between the I.R. spectra of niobium pentafluoride obtained by Beattie et al [40] for a powder sublimed onto a silicon plate cooled to -196°C, and that obtained by this author, are more difficult to explain. It is possible that absences of some bands in the higher regions of this spectrum

TABLE 1:3:1

Raman spectra of solid and liquid NbF_5 abd TaF_5 (all frequencies in cm^{-1}, band intensities given by letters or numbers in brackets).

NbF_5(s) (40)	NbF_5(s) (38)	NbF_5(s) This work	TaF_5(s) (40)	TaF_5(s) This work	NbF_5(l) (40,41)	TaF_5(l) (40,41)
	.820(3)					
766vs	773(10)	765(125)	757vs	756(120	767s,p	752vs,p
752w		754(25)	727m	727(20)	726w≠	713w
716vs	724(5)	716(70)	694ms	697(50)	683m,p	690w,p
668w	669(2)	673(5)	671w			
656m		656(30)	646mw			
270ms	266(6)	267(50)	273ms	271(60)	(315w)*	(312w)+
252vw			254w		253m	245m
238vw			236m	237(20)	226m	213sh
226w			221vw			
182w			183w		(180)*	(184w)*
763w	168(1)					
130w	146(1)		119vw		136w	121w
			106			

* These bands were not found by Selig et al (41)

\+ These bands were not found by Beattie et al (40)

(s) Indicates solids, (L) indicates liquids p= polarised.

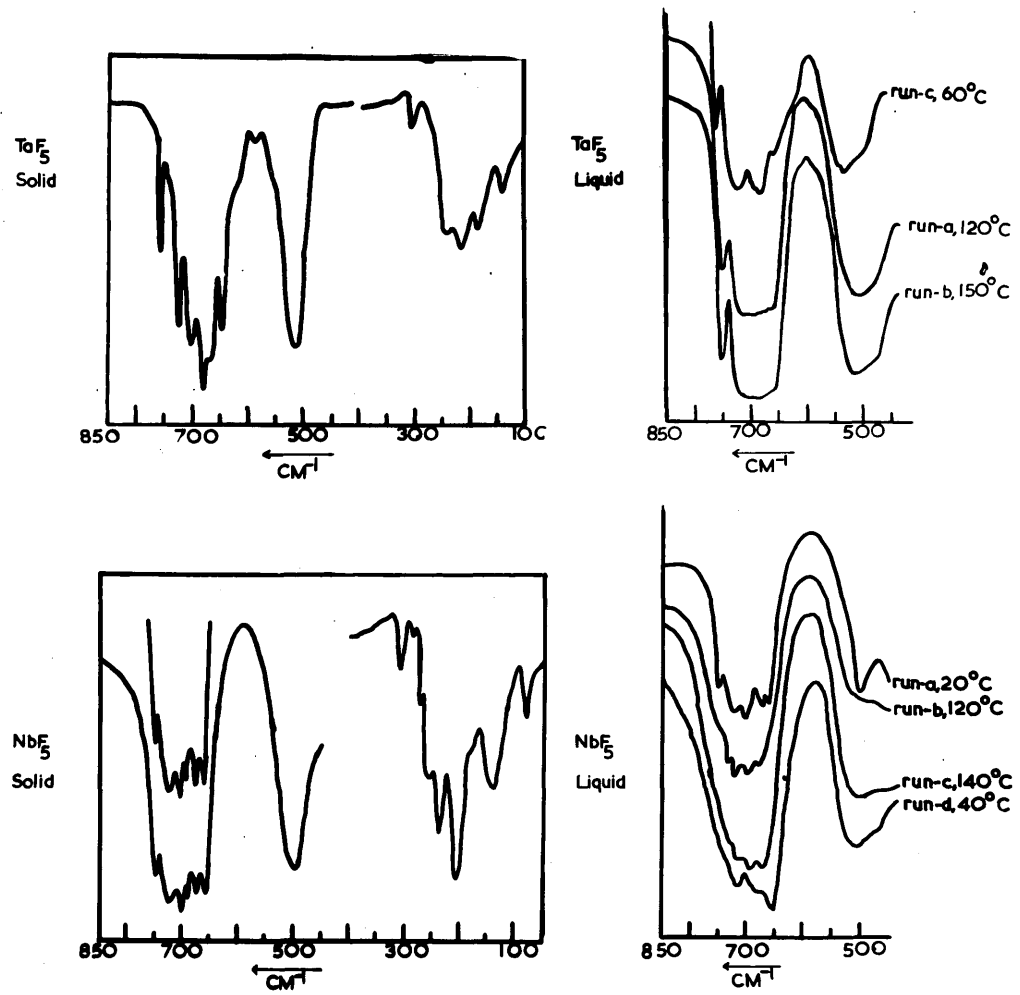


Figure 1:3:1 I.R. Spectra of Pentafluorides

TABLE 1:3:2

I.R. spectra of Solid Pentafluorides (all frequencies in cm^{-1})

NbF_5 (41)	NbF_5 (39)	NbF_5 This Work	NbF_5 (41) calc‡	TaF_5 (39)	TaF_5 (43)	TaF_5 This Work	MoF_5	MoF_5 (44)
734vs		746s	749(22)	752s	750m	754ms	763vs	745vs
		721vs	746(25)			721vs	736ms	
		700vs				698s	722m	698vs
688s		692sh		675s		674s	710m	
		672s	662(27)			667sh	696vs	
661m	650s	660s		637s	645s,b	644ms	650bsh	647vs
514ms						585vw		
479w	486s,b	498s,b	478(28)	507s,b	515s,b	511b,s	510b,m	520m
378vs								480w

Continuation/

320m					377vw			
303vw	304w	300m	269(23)	305w	310w	310w	307w	
279m		255sh	266(29)	280vw	253vs		250sh	
246w		235s	255(30)	242m	235vs	232sh	230s	200m
		213sh	241(24)	219m	220vs	216s,b		
204vw	203m	202vs	205(31)					
	185sh	170sh	167(32)	185m		187m		166m
	131w	132s	121(33)	135w		138		
		81m	74(34)					

‡ Numbers in brackets correspond to mode descriptions as follows
22- Nb-F ax Str.(A_{2u}), 25- Nb-F eq Str.(e_u), 26-Nb-Fe q Str.(e_u), 27-Nb-Fax Str.(e_u), 28-Nb-F-Nb. br. Str.(e_u), 23-Nb-F eq Wag (a_{2u}), 29,32,33,34-mixed (e_u), 30-Nb-Fax Bend (e_u), 24-Nb-Fax rock (a_{2u}), 31 Nb-F eq bend (e_u).

The calculated numbers are presented for comparison and are not meant to imply assignment of observed bands.

(e.g. those at 721 and 700 cm^{-1} - see table 1:3:2) and shifts in some other bands (e.g. the band at 514 cm^{-1} is 16 cm^{-1} higher than that found by this author) are due to the use of silicon plates which absorb strongly, and non-uniformly, in the region 450-1300 cm^{-1}. A very strong band at 378 cm^{-1} is present in Beattie's spectrum of NbF_5 which is absent in the spectra of Preis, and of this author. It is suggested that this peak must be attributed to hydrolysis products.

Figures of the I.R. spectrum of TaF_5 as a nujol mull published in reference (42) show the peaks at approximately 515 and 645 cm^{-1} to be poorly resolved. The spectrum is otherwise in reasonable agreement with this work and a weak peak at 377cm^{-1} is again attributed to hydrolysis. Differences between the published I.R. spectra of solid MoF_5 (43), and that of this author are attributed to differences in mulling technique, although a weak band at 480 cm^{-1} in the published spectra may be due to impurities.

In this work the similarity of I.R. spectra obtained using KBr, AgCl, Si, and Ge windows, and the lack of change in the I.R. spectra of NbF_5 heated to 140° with nujol indicate that little or no reaction with window materials, or nujol occurs so long as water and unsaturated hydrocarbon impurities are removed.

Because of experimental difficulties the I.R. spectra of liquid niobium and tantalum pentafluoride could not be obtained

under such rigorously dry conditions as the spectra of solid pentafluorides. Weak peaks, attributed to hydrolysis, and observed at 1020 cm^{-1} at room temperature disappeared and medium weak bands appeared at approximately 950 $cm.^{-1}$

In preliminary experiments in the present work on the solid spectra of niobium, tantalum and molybdenum pentafluorides weak peaks were observed at approximately 1020 cm^{-1} and ascribed to hydrolysis, but there were no changes in the I. R. spectra of other regions. It is concluded that the I.R. spectrum of the liquid pentafluorides is probably not affected by hydrolysis in the region 800 - 400 $cm.^{-1}$

Differences between Raman spectra of niobium and tantalum pentafluorides obtained by this author, and those in the literature [38,40] are almost certainly mainly due to differences in instrumentation. The Raman spectrometer used in reference (41) was fitted with an argon ion laser probably giving 700 m watts of energy at the sample. The Cary 81 used in this work was fitted with a helium-neon laser giving 30-40 m watts of energy at the sample and with these samples no spectra could be obtained when the Raman shift was less than 220 $cm.^{-1}$ The Raman line reported at 820 cm^{-1} [38] in NbF_5 may be due to an impurity in the sample used as no band was found, either by this author, or by Beattie et al [40] in this region.

The tetrameric [45] molecules of solid niobium, tantalum

and molybdenum pentafluorides have D_{4h} symmetry. In the isolated molecule there are sixty six internal modes of vibration of which thirty two are in sixteen degenerate pairs. The modes have the following species and activities:-

$6a_{1g}$ (R) + $4a_{2g}$ (i) + $6b_{1g}$ (R) + $5b_{2g}$ (R) + $6e_g$ (R) + $2a_{1u}$ (i) + $4a_{2u}$ (I.R.) + $3b_{1u}$ (i) + $4b_{2u}$ (i) + $10e_u$ (I.R.),

(i), (R), and (I.R.) indicate inactive, Raman active, and I.R. active respectively, giving a total of twenty three raman and fourteen I.R. active fundamentals. In the crystals, which have space group $C_{2/m}$ [45] the symmetry of the molecule drops to C_{2h}. In this environment all the "g" modes and "u" modes of the D_{4h} environment are formally Raman and I.R. active respectively. The "e" modes are all split so thirty three Raman and thirty three I.R. bands are formally expected. Because there is only one tetrameric unit per primitive unit cell [45,46] the position is not further complicated by "factor group" splitting.

For tantalum pentafluoride thirteen I.R. and twelve Raman bands are found, for niobium pentafluoride fifteen I.R. and twelve raman bands are found, and in both cases the poor quality of the I.R. spectra below 400 cm^{-1} probably conceals more bands (see tables 1:3:1, 2, and figures 1:3:1 a,b) The overall superfluity of I.R. bands, over the number predicted for a D_{4h} tetramer, and the presence of six bands in the region 640-770 where four are predicted [40] suggest that the approximation of D_{4h} symmetry, implied in the simplified vibrational analysis of

Beattie et al[40], is not completely valid, although the overall predicted energies are unlikely to be much affected. Both the experimental vibrational spectra of NbF_5, TaF_5 and MoF_5 and the simple vibrational analysis[40] of niobium pentafluoride suggest that vibrational spectra of these pentafluorides may be divided into three regions:- a metal-terminal fluorine stretching region (600-800 $cm)^{-1}$, a metal-bridging fluorine stretching region (450-550 cm^{-1}) and a metal-fluorine angle deformation region (50-350 cm^{-1}). The different types of quite different energies and mixing of modes of different types will probably have little effect on their energy.

I.R. bands which can be assigned to metal bridging fluorine stretching modes are found in the I.R. spectra of $NbCl_4F$, and $TaCl_4F$, which are tetrameric with fluorine bridges similar to NbF_5 and TaF_5[45,47,48] at 485 and 495 cm^{-1} respectively. The similarity of the bands of tetrachloride fluorides, and pentafluorides provides further evidence that these bands are due to metal-fluorine bridging modes and that their energy is not greatly affected by coupling to other modes.

An important consequence of the separation of vibrational spectra of pentafluorides into regions involving different modes is that I.R. spectra may, in certain circumstances, be used as a diagnostic test for the presence of bridging and terminal fluorine atoms. Raman spectra are not so useful because metal fluorides are weak Raman scatterers and the stretching modes of symmetrical M-F-M-bridges are expected to be very weak Raman scatterers. This latter is because on movement of the fluorine

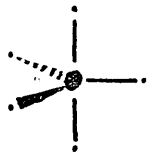
atom the increase in polarisability at one metal atom is matched by a decrease in that of another metal atom and the overall change in molecular polarisability is small.[40]

The structure of liquid pentafluorides has been the subject of some discussion. Polymeric structures have been suggested for niobium and tantalum pentafluorides on the basis of viscosity,[49,50] and Raman[40] measurements, whilst Raman measurements have also been quoted as evidence that niobium[41], tantalum[41] and molybdenum[43] pentafluorides are all monomeric with D_{3h} symmetry in the melt. It is the view of this author that Raman spectra can provide little information relevant to this problem.

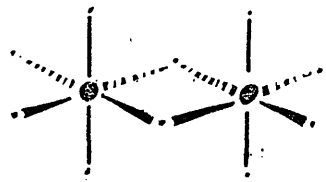
It is first necessary to consider all the structural possibilities for these pentafluorides in the melt. A selection of the more reasonable structures are shown in figures 1:3:2 a - h.

Of these structures "h" may be ruled out immediately because there are no strong I.R. absorptions in the region 570-620 cm^{-1} in the liquid spectra where MF_6^- ions are known to absorb strongly, and conductivity measurements suggest that self ionisation of niobium and tantalum pentafluorides is less than 1%[49,50]

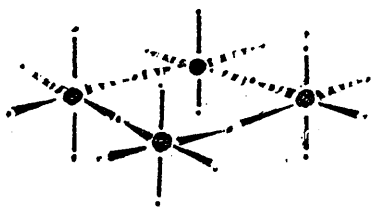
Group theoretical studies of I.R. and Raman activities indicate that in all the cis, and trans-linked oligomers of MF_5 units involving pseudo-octahedral coordination there should be formally active metal-bridging fluorine stretching modes and



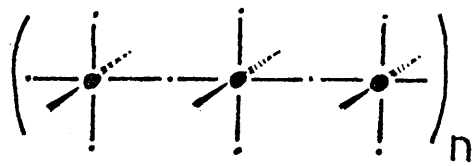
a) D_{3h} Monomer



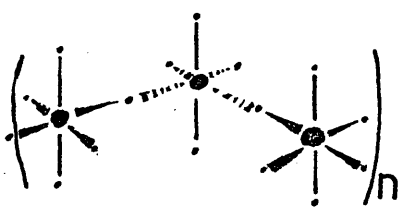
b) Dimer



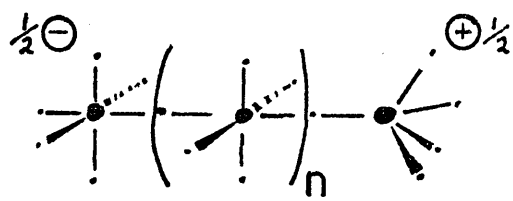
c) Tetramer



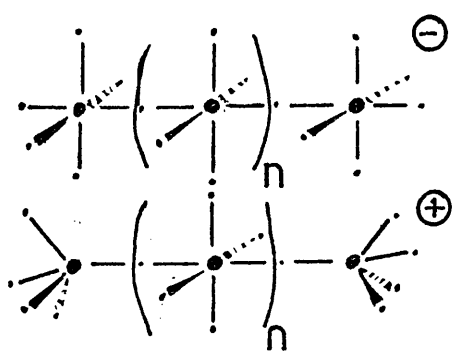
d) Infinite "trans" polymer



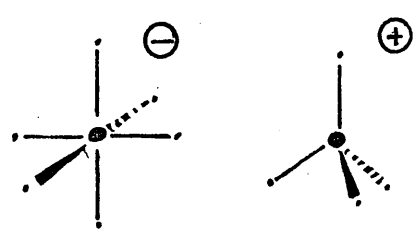
e) Infinite "cis" polymer



f) Heteropolar "trans" polymer (also "cis" version)



g) "Trans" polymeric ions (also "cis" version)



h) Simple ions

Figure. 1:3:2(a-h), Possible structures of MF_5,(M=Nb, Ta,Mo) in the melt.

●=Nb •=F

metal-terminal fluorine stretching modes. (see e.g. Appendix 2)

Niobium, antimony [51], and molybdenum pentafluorides as well as the trans-bridged bismuth pentafluoride [52] and niobium and tantalum tetrachloride fluorides [38] and other bridged fluorides all show an I.R. band attributable to a metal-bridging fluorine stretching mode. Only SbF_5 [53] gives a Raman band in this region, which may be due to deviation from linearity in the Sb-F-Sb bridging bonds.[54] It is thus not possible to detect bridged species in liquid pentafluorides by Raman spectra alone.

It may be considered proved by induction that in all cases where octahedrally coordinated, five valent, central atoms are linked by fluorine atoms there will be I.R. active modes corresponding to metal-bridging fluorine stretching modes with frequencies approximately 65-75% of the frequencies of central atom - terminal fluorine stretching modes. The spectra of monomeric arsenic,[55] and vanadium [56] pentafluorides suggest that there is no such distribution of I.R. bands in D_{3h} species, although ν_4 is at lower frequencies than the totally symmetric stretching modes. In all cases metal-terminal fluorine stretching modes were present in both I.R. and Raman spectra.

The presence of a strong peak in the reported I.R. of liquid MoF_5, [43] at approximately 500 cm^{-1}, and similar peaks found in liquid NbF_5 and TaF_5 in this work (see figs 1:3:1 c, d) is considered indicative of bridging fluorine atoms. The frequencies

of these peaks are too high to be associated with ν_4 of a D_{3h} monomeric species as was previously suggested. (43)

The Raman spectra of liquid niobium, tantalum, and molybdenum pentafluorides are different from those of the solids, (40,41,43) and the peaks are broader. This suggests that the tetrameric rings are broken. The greater linewidth of Raman bands in the melt could be due to rotational isomerism in the polymers, interactions between oligomeric ions, or a large dispersion of molecular weights in oligomers present. In view of the absence of tetramers in the melt it is unlikely that other cyclic oligomers represent a large proportion of the material present in the melt. It is not possible to tell from vibrational spectra whether the oligomers present in the melt are of cis, or trans configuration, or whether they are ionic or not. Conductivity data (49,50) does not prove the presence of ions because the heteropolar open chain structure (fig 1:3:2f) can act as a conductor by dissociating at the electrode. This conductivity suggests, although not conclusively, that structure "g" is not predominant unless the ions have a very high molecular weight (MW> 10,000)

The presence of only one detectable resonance in the ^{19}F N.M.R. spectra of liquid niobium and tantalum pentafluorides is consistent with either fast intermolecular or intramolecular exchange, but the presence of only one line in a mixture of the two suggests a low activation energy for intermolecular exchange. It is not possible to gauge the rate of exchange because of

quadrupole broadening of the ^{19}F resonances observed.(57) In view of the low conductivity of NbF_5 and TaF_5 melts N.M.R. data suggests that the melt contains open-chain species (fig 1:3:2f).

NbF_5 and TaF_5 are only slightly soluble in solvents with which they do not react irreversibly. Solutions of NbF_5 in benzene and tungsten hexafluoride gave no ^{19}F N.M.R. attributable to niobium fluorides although the tungsten hexafluoride solution was approximately 10% NbF_5. The slow rate of reaction of NbF_5 with anisole, even in solution, implies a significant activation energy to reaction. This activation energy probably does not arise from steric factors in the anisole and pentafluoride monomers, or open chain oligomers should not show significant activation energies to adduct formation. The evidence thus suggests that the tetrameric unit is retained in solution at room temperature.

The published I.R. spectra of niobium pentafluoride in the vapour phase at 100-140°C is consistent with the presence of polymers.(39) The original interpretation of the spectra seems invalid as the band found at 510 cm^{-1} is too high to be associated with ν_4 of a trigonal bipyramid as suggested. Two bands at 748 and 732 cm^{-1} were assigned to P, and R branches of ν_5. It is not clear why the Q band should be missing (40) or the NbF_5 molecule should have been assumed to have such a small moment of inertia.

Mass spectra of niobium pentafluoride produced no evidence for polymers in the gas phase. However this is not proof that they do not exist. An attempt was made to keep both the heated

sample inlet tube and ionisation chamber below 70°C but this may not have been successful. In a comparable mass spectroscopic study of antimony pentafluoride at 25°C the intensities of $Sb_2F_9^+$ peaks were only 0.44% of those for SbF_4^+ (58) It is known from vapour pressure measurements that antimony pentafluoride is polymeric in the gas phase (55) $(SbF_5)x$ at 150°, 180°, and 250°C x=3, 2.7, and 2 respectively. Breakdown reactions of polymeric cations, e.g. $Nb_2F_9^+ \longrightarrow NbF_5 + NbF_4^+$, may be faster than breakdown of neutral species. Negative ion mass spectrometry would be more likely to detect polymeric species.

Three additional, recent publications on the state of niobium, tantalum, and molybdenum pentafluorides in liquid and gaseous phases are worthy of note:-

The observed electron diffraction patterns (59) of niobium pentafluoride are not consistent with either NbF_5 monomers, or Nb_2F_{10} dimers. The divergence from calculated monomeric diffraction is smallest at high temperatures and the results are consistent with a temperature dependent equilibrium involving at least one type of polymeric molecule.

Magnetic measurements of molybdenum pentafluoride (60) as a solid and liquid over a variety of temperatures have shown a discontinuity in magnetic behaviour at the melting point. This indicates that the tetramers of the solid state are not retained in the liquid. The results obtained were not consistent with the presence of monomers in the liquid state

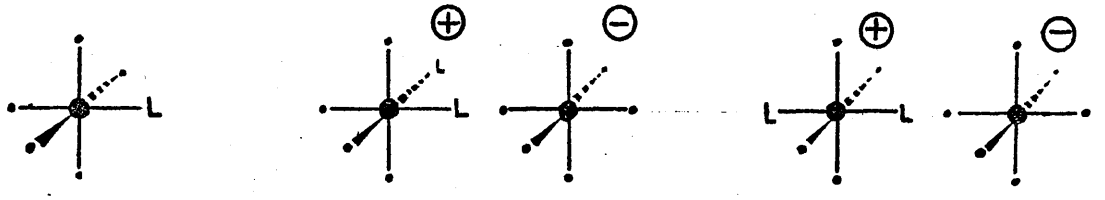
Molecular beam-mass. spectroscopic experiments have detected M_3 fragments above melts of niobium and tantalum pentafluorides.[61] Curiously the proportion of polymeric fragments found above pentafluoride melts increased along the periodic table and pentameric fragments were found above iridium pentafluoride melts. The results are consistent with the presence of open-chain polymers in pentafluoride melts. The absence of fragments higher than trimers of NbF_5 and TaF_5 does not exclude the possibility of their presence.[62]

Summary

The vibrational spectra of niobium, tantalum and molybdenum pentafluoride may be satisfactorily divided into three regions, a terminal fluorine-metal stretching region, a bridging fluorine-metal stretching region, and fluorine-metal bending region. The I.R. bands in the bridging fluorine region may be used as a diagnostic test for bridging fluorine atoms. NbF_5, TaF_5, and MoF_5 are thus judged to be polymeric in both liquid and vapour state although the tetrameric structure of the solid is not retained. An open-chain, non-ionic, polymeric structure (see fig 1:3:2f) is consistent with all published information on the liquid NbF_5, TaF_5 and MoF_5 systems.

1:4 Stereochemistry of 1:1 and 1:2 complexes of Metal Pentahalides in the Solid State.

The possible structures of 1:1 complexes include those shown in figures 1:4:1a,b and c and a large number of structures involving seven and eight coordinate metal atoms linked by bridging halogen atoms.



a structure — b ionic structure — c ionic structure

cis cation — trans cation

Figure 1:4:1 Structure of 1:1 pentahalide complexes

● = halogen ● = metal L = base.

The 1:1 complexes of niobium, tantalum and molybdenum pentafluorides show no I.R. bands in the region 400-510 cm^{-1} which suggests that no bridging fluorine atoms are present.

The possible structures for 1:2 pentafluoride-base complexes include those illustrated in figures 1:4:1a,b, and c with some free base incorporated in the lattice, ionic structures containing MF_6^- and $MF_4L_4^+$ ions, and a variety of structures involving seven

TABLE 1:4:1

FACTOR GROUP ANALYSIS

$KNbF_6$-D_{2d}^6 N°116			$C_2'' \rightarrow C_2'$	$C_2 \rightarrow C_{22}$	$C_{2x} \rightarrow C_2$	
Mode	Species O_h	Species D_{4h}	Distorted ion 2d	Site Group D_2	Factor Group D_{2d}	Activities
1	A_{1g} (R)	A_{1g}	A_1	A	$A_1 + B_1$	R
2	E_g (R)	A_{1g}	A_2	B_1	E	1R R
		B_{1g}	B_1	A	$A_1 + B_1$	R
3	F_{1u}	A_{2u}	B_2	B_1	E	1R R
4	(1R)	E_u	E	B_2 +B_3	E	1R R
					A_2 +B_2	i 1R R
5	F_{2g}	B_{2g}	B_1	A	$A_1 + B_1$	R
		E_g	E	B_2 +B_3	E	1R R
					A_2 +B_2	i 1R R
6	F_{2u}	B_{2u}	A_1	A	$A_1 + B_1$	R
		E_u	E	B_2 +B_3	E	1R R
					A_2 +B_2	i 1R R

$CsNbF_6$ - C_3^2 N°148			
Mode	O_h	T_h	S_6
1	A_{1g}	A_g	A_g (R)
2	L_g (R)	E_g	E_g (R)

Mode	O_h	T_h	S_6
3&4	F_{1u} (1R)	F_u	A_u+E_u (1R)
5	F_{2g} (R)	F_g	A_g+E_g (R)
6	F_{2u} (i)	F_g	A_u+E_u (1R)

coordinate metal atoms. No evidence was found for any uncoordinated base in the 1:2 complexes (see section 1:6)

If hexafluormetallate ions are present in these compounds there should be I.R. and raman bands corresponding to those ions. The vibrational spectra of $KNbF_6$, $KTaF_6$ and $KMoF_6$[63] which have the crystal structure D_{2d}^6, N°116,[64,65] and $CsTaF_6$[42,66] and $CsNbF_6$[67] which have the crystal structure $C_{3i}^2 \equiv S_6^2$, N°148[65,68], have been studied but have never been analysed in the light of a proper factor-group analysis, or the probable optical properties of the compounds. The factor group analysis, performed by the method of Halford,[69] and given in table 1:4:1 for octahedral, and pseudo-octahedral ions present in D_{2d}^3 and C_{3i}^2 crystals has been checked by the method of Adams and Newton.[70] Correlation tables used were those of Wilson et al[71] except for the $C_{2x} \longrightarrow C_2$ correlation of site group D_2 with Factor group D_{2d} which was worked out (The need for this was pointed out by J. Dunsmuir).

The relative size of these splittings is difficult to predict with accuracy, and may not be the same for all modes. The most common order of size of splittings is distortion > site group > factor group but in these cases some modes will be completely unaffected by distortion of the hexafluoro-metallate anion.

A further cause of complications becomes evident in the I.R. spectra. The refractive index of a material changes in the region

of an I.R. absorption band. If the mode is associated with a large dipole change, it absorbs very strongly, and may also become what is known as a "strong oscillator[72] these are associated with large changes in refractive index over large frequency ranges. In these ranges large losses of light are caused by scattering, the bands observed are not purely absorption bands, and the observed νmax of an I.R. band is not, necessarily, the true vibrational frequency of the molecule or ion, which tends to be at higher frequencies than νmax. Strong oscillator effects are not observed in dilute systems and may also be allowed for by recording reflectance I.R. spectra. No reflectance, or solution I.R. data for these hexafluoromellate ions is available.

The following bands have been observed in niobium, tantalum, and molybdenum hexafluoride ions:- (all frequencies in cm^{-1})

$CsNbF_6$ Raman[67] 683,s, 562,w, 280,b,m.

$CsTaF_6$ Raman[66] 692,s, 581,w, 270b,m.

I.R.[42] 720m, 582vb,asg,vs,480m 245sh,s,232s,220sh,s

$KNbF_6$ I.R.[63] 580s

$KTaF_6$ I.R.[63] 580s

$KMoF_6$ I.R.[63] 623s

By comparison with hexafluorides the following bands and activities are expected in isolated octahedral anions:-

ν_1(R) 680-700 cm^{-1}, ν_2(R) 550-590 cm^{-1}, ν_5(R) 260-300 cm^{-1}, ν_4(I.R.) 210-240 cm^{-1}, ν_3(IR) 560-650 cm^{-1}, ν_6(inactive) 100-240 cm^{-1}(metal dependent)

It is unfortunate that only two Raman spectra of these hexafluorometallate ions have been reported, because Raman spectra are not subject to strong oscillator effects and present an easy method to study both site-, and factor-group splitting and the effect of cationic size on the hexafluoride anion frequencies. In the $CsNbF_6$ and $CsTaF_6$ systems ν_5 is the only Raman active band expected to show site group splitting. Although Keller et al only report one Raman band in the region 240-300 cm^{-1} for $CsNbF_6$[66] and $CsTaF_6$[67] their diagrams[66,67] clearly show the bands at 270-280 cm^{-1} in $CsNbF_6$, $CsTaF_6$ to be broad and asymmetric, consistent with a splitting of about 20 cm^{-1}

The reported I. R. spectrum of $CsTaF_6$[42] contains six bands but this author suggests that the published assignments are incorrect. In a C_{3i}^2, (S_6^2) environment both ν_3 and ν_4 of TaF_6^- are split into Au and Eu components. Baum et al assign a very strong band at 580 cm^{-1}, together with medium bands at 720 and 480 cm^{-1} to ν_3 stating that anharmonicity may have lifted the degeneracy of the Eu component to give a total of three components. This author would assign the band at 720 cm^{-1} to nujol, and that at 480 cm^{-1} to an impurity, or an overtone or combination enhanced by fermi resonance. The site group splitting of ν_3 contributes to the asymmetry of the broad band at 580 cm^{-1}

The group of bands at 220,250 cm^{-1} has a total half-band width of about 50 cm^{-1} and probably does not exhibit strong oscillator

effects. Again splitting of the Eu component is discounted by this author and it is suggested that one of the shoulders is due to ν_6 which is I.R. active under S_6 symmetry.

The values of ν_3 reported for the potassium hexafluoro-metallates [63] are even more dubious than that of $CsTaF_6$ for, as shown in the factor group analysis, there are three I.R. active components of ν_3, and no splitting was observed although the ion shows distortions observable by x-ray diffraction[64]. The band observed must have been greatly broadened by strong oscillator effects and the recorded νmax is not the true oscillator frequency.

The true values of ν_3 are almost certainly higher than those quoted in the literature, but it is not possible to say how much higher. If MF_6^- anions were present in the 1:1 and 1:2 complexes of pentafluorides the cations would be far larger than alkali metal ions so that the system would be effectively diluted and strong oscillator effects would be reduced with respect to alkali metal hexafluorometallates. Thus values of ν_3 for MF_6^- ions observed in these complexes would be higher than those recorded above if MF_6^- ions were present.

The 1:2 pentafluoride complexes with pyridine, with crystal type $P2_1/m$ (No 11), are the only pentafluoride complexes of known crystal type. In all the environments, C_i, C_2, C_1, which the MF_6^- ions could take up in these lattices [70] some components of all six modes are active in both I. R. and Raman, and all the

observed bands should be split. The bands ν_3 and ν_4 would be expected to remain the strongest I.R. bands and ν_1, ν_2, and ν_5 should remain the strongest Raman bands. Similar considerations probably apply to all the other solid complexes as it is unlikely that they constitute a lattice of high symmetry. In all the complexes I.R. bands were found which might correspond to ν_3 and ν_4 if only one compound were to be considered (Tables 1:4:2, 1:4:3). However there is little difference between the frequencies which might be associated with ν_3 for pentafluoride complexes of molybdenum, tantalum, or niobium with the same base, whilst a large difference (40-45 cm^{-1}) is found in the hexafluorometallates. The observed frequencies of the 1:1 and 1:2 complexes are more base-dependant than would be expected in ionic structures. (See tables 1:4:2, 1:4:3), which, if complexes of the same stoichiometry are assumed to have similar structures, suggest that the complexes are not ionic.

Because no work has been done on comparison of Raman shifts of hexafluorometallate anions with different cations it is not known how large the variations may be. In most of the complexes Raman bands were found which might have corresponded to the strong ν_1 (680-700 cm^{-1}) and medium ν_5(260-290 cm^{-1}) bands of an MF_6^- ion. However no bands were found which might correspond to ν_2(562 cm^{-1} in $CsTaF_6$) in any of the tantalum compounds. Although this is not a strong band it is felt that such a band should have been observed if MF_6^- ions were present. In the

TABLE 1 : 4 : 2

Bands in the vibrational spectra of 1 : 1 complexes attributed to metal-fluorine modes in the range 300-800 cm^{-1} (all values in cm^{-1}; Raman intensities in brackets)

$NbF_5.Me_2O$		$NbF_5.CH_2ClCN$		$NbF_5.CH_3CN$		$NbF_5.CH_3CH_2CN$		$NbF_5.Me_2SO$	
I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman
709m	695(90)	719s	714(12)	710s	702(20)	710s	702(200)	721mw	
674sh									
666vs	664(20)	660vs	684(14)	660s	673(3)	666s	668sh	664ms	665(15)*
643shs		625vs		638s		638s		625vs	
	594(10)				592(2)		596(10)	605vs	

$TaF_5.Me_2O$		$TaF_5.CH_2ClCN$		$TaF_5.CH_3CN$		$TaF_5.CH_3CH_2CN$		$TaF_5.Me_2SO$	
I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman
722ms		715s	712(40)	712vs	710(30)	708s	not	722m*	
710w*									
670w		669ms	673(30)	655m		657sh	scanned	677m	673(15)*
630s									
	614(65)	608vs	609(15)	612sb		615vs		582s	

$TaF_5.Me_2SO-d_6$		$MoF_5.CH_2ClCN$		$MoF_5.CH_3CN$		$TaF_5.2MePy$		WF_5Cl	
I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman
681)*		710m	706(200)	703mw	697(90)	698s	not	743s(1)	744s
676)s	672(10)*	660s,b	679) (15)	650vs	665(5)			704m(2)	703m
	638(10)*	630s	670)	635sm		609vs	scanned	670s(3)	661m
586vs						590sh		640s(5)	644w

*may be ligand bands

Table 1:4:3, Vibrational spectra of 1:2 pentafluoride complexes (all Raman intensities in brackets)

$NbF_5.2Py$		"$NbF_5.(4MePy)_2$"		$NbF_5.2Me_2SO$	
I.R.	Raman	I.R.	Raman	I.R.	Raman
290b,sh		240s		240m 265sh	
343m		346s		330m 358m	not
563b,s				555m	scanned
584w	588(40)	568m		579m	
602s,b		607vs,b	600(4)	603s,b	
614s,b,as	640(30)		610(10)	610sh	
	676(50)		665(40)*	635sh	
	687(100)		686(50)*	722ms	

$TaF_5.2Py$		$TaF_5.(D_5Py)_2$		$TaF_5.(4MePy)_2$	
I.R.	Raman	I.R.	Raman	I.R.	Raman
	145(w)		160w	240 m	140(15)
	180(w)				
	190(w)				
	240(30)	245sh	230w		260(8)
	280(45)		280m		285(5)
330m	320(w)	328ms		298w	300(8)
585vs,b		532m		332ms	
	603(60)	570sh	595(50)	578)vs	615(90)
	645(45)	590vs,b	625(90)	584)	670(50)*
	693(40)		688(10)		687(40)

"$NbF_5.2NHMe_2$"		$TaF_5.2NHMe_2$		$TaF_5.2Me_2SO$	
I.R.	Raman	I.R.	Raman	I.R.	Raman
				240 s	
				260m	
				310ms	
				331w	
				359m	
552m	560(3)	551vs,b,asy		580vs	
592mw	587(w)	566vvs,b,asy		670w	604(30)
609s,asy,	678(7)	639ms	640(100)	693s,asy	691(140)
	678(7)			722m	723(30)*

* may be ligand bands

niobium and molybdenum pentafluoride complexes some Raman bands were observed in the 580-600 cm^{-1} region, but it is thought that they showed too much variation to be considered MF_6^- frequencies. Thus this Raman evidence also suggests that no MF_6^- ions are present in pentafluoride complexes of the solid state.

The structure of WF_5Cl is similar to that shown in fig. 1:4:1 a. Group theory predicts four Raman bands, of which three are I.R. active for WF_5Cl in the metal-fluorine stretching region. The bands found [73] (see table 1:4:2) in the gas and liquid phases are consistent with the predictions. In the solid phase the fourth Raman band (ν_5) becomes I.R. active. In many of the 1:1 complexes only 3 I.R. bands are found in the metal-fluorine stretching region, but this is to be expected as the complexes are probably not isomorphous. Taken together the vibrational spectra of the 1:1 complexes strongly suggest that they have approximately C_{4v} symmetry (cf Fig. 1:4:1 a)

The I.R. spectra of all the bases used in this work show changes upon coordination to an acid. In none of the 1:2 complexes investigated was any uncoordinated base detected. This is important because no evidence has ever been published to show that both molecules are coordinated to the metal. Little more can be said of the 1:2 complexes of NbF_5, TaF_5 and MoF_5. Although the I.R. and Raman spectra suggest they are not ionic. The evidence is not as conclusive as in the case of the 1:1 complexes. N.Q.R. spectra of $NbF_5 \cdot Py_2$ did not give any unambiguous

TABLE 1:4:4

Vibrational spectra of pentachloride complexes (values in cm^{-1} Raman intensities in brackets.

$NbCl_5$ .ClH_3CN Raman	assignment *	$NbCl_5.Me_2S$ I.R.	Raman	$NbCl_5.OEt_2$ I.R.	Raman	$NbCl_5.Py$ I.R.	Raman	$NbCl_6^-$ I.R.	Raman ‡
397(24)	NB-Cl_{xq} a_1	395sh	381(250)	389sm	384(150)	408s	420(30)		
377(15)	)	372vs a	368(15)	368vs		378sh			
372(7)	) Nb-Cl qe				356(50)	355) b	361(50)		
						)			ν_1
354(1)	Nb-Cl_{xq} a,			355vs	3.	345) vs		ν_3	330-360.
347(0.5)						335)		333-	
300(3)	Nb-Cl_{xq} b,		299(10)		298(14)			336	ν_2 260-300
279vw				279sh		280b sh			
246(1)	ν mixed e_1							ν_4 ≏ 270 h.o.	
220vw *									ν_5
192(7)	Nb-Cl a_1		185(20)						150-180
172(sh)									
164(5)	ν mixed e				161(20)				
158(2)	NbCl b_2		155(15)						
127(3)	ν mixed		146(20)						
115(6)	b,								
80(sh)	ν mixed e								
59(2)									

q = equatorial x = axial

* reference 74

‡ Values by comparison with other hexachlorides

results (see Chapter 3) and further conclusions about these compounds must await single crystal x-ray analysis.

The I.R. and Raman spectra of pentachloride complexes of niobium show similarities to the spectra of 1:1 pentafluoride complexes (Table 1:4:4). It is not possible to separate all the bands in the metal-chlorine stretching regions. Vibrational analysis of $NbCl_5 \cdot CH_3CN$ has been attempted twice since this work was started [74, 120] and provides evidence in support of conductivity data [36] that the adducts may be formulated as non-ionic six-coordinate monomers. Hexachloroniobates [76,77] show I.R. absorption bands between 333 and 336 cm^{-1} not found in $NbCl_5$ complexes which is further evidence that the complexes are not ionic.

As in the pentafluoride complexes the bands in the metal-halogen stretching region of pentachloride complexes show some sensitivity to change of coordinated base. There is, however no obvious pattern to the shifts. The assignments of Raman bands of $NbCl_5 \cdot CH_3CN$ are those of Ozin and Walton [74]

There are considerable differences in the number of bands found in the Raman spectra of these pentachloride complexes. This is thought to be due to differences in refractive indices of the compounds which are known to have an effect on the quality of Raman spectra.[75] 1:3 Stereochemistry of pentafluoride adducts in the vapour and liquid phases and in solution.

Evidence relating to these systems is very limited. The

complexes with Me_2O, and CH_2ClCN are more volatile than the corresponding pentafluorides, suggesting considerable acid-base association in the gas phase. The absence of ions in the mass spectra which could not have been derived from separate pentafluoride and base molecules is not proof of dissociation.

In the liquid phase the I.R. spectra, due to M-F frequencies of $NbF_5 \cdot OEt_2$, $TaF_5 \cdot OEt_2$, and $NbF_5 \cdot CH_3OC_6H_5$, are similar, in the range 250-750 cm^{-1}, to those of other, solid, 1:1 complexes. ^{19}FN.M.R spectra of liquid 1:1 pentafluoride complexes indicate the presence of some exchange phenomena which averages the ^{19}F environment. In contrast to these systems NbF_5Cl^- (78) WF_5OR, (79) and WF_5Cl (80) and many other C_{4v} systems exhibit the expected quintet-doublet resonance pattern. If the exchange processes were intramolecular, or involved fluorine bridges there would be no obvious reason for absence of exchange phenomena in the WF_5Cl, NbF_5Cl^- systems. It seems most likely that exchange occurs by a mechanism involving cleavage of metal-base bond which is in agreement with the observed averaging of ^{1}H.N.M.R. spectra in the presence of excess base.

Surprisingly Raman spectra of solutions of $NbF_5 \cdot CH_3CN$ in CH_3CN suggest presence of a 1:1 C_{4v} complex despite Raman evidence that a 1:2 adduct is present in a 1:2 stoichiometric mixture of NbF_5 and CH_3CN (Table 1:6:11) and the claimed isolation of complexes $NbF_5 \cdot (CH_3CN)_2$ (37) and $MoF_5 \cdot (CH_3CN)_2$ (43). In contrast the I.R. spectrum of a mixture MoF_5, and CH_2ClCN containing 30

mole% of MoF_5 seems to indicate the presence of a 1:2 complex in solution (Table 1:6:12)

No ^{19}F N.M.R. spectra of pyridine and methyl pyridine adducts in excess ligand could be obtained because of small solubility of the adducts. All the 1:2 complexes investigated showed signs of decomposition when melted. It is unlikely that these compounds can be obtained in the gas phase.

1:6 Some Chemical aspects of reactions of pentahalides with bases and vibrational spectra of complexed bases.

A) Reactions and spectra of pentafluorides with ethers.

Although some metal fluorides react with ethers to give oxyfluorides (32), satisfactory analytical data for all the ether complexes except tantalum pentafluoride dimethyl etherate, (which gave I.R. data similar to corresponding niobium compound), and the absence of any I.R. absorptions in the 900-1050 cm^{-1} region, indicate that no fluoride elimination has occurred. Contrary to literature reports (30) niobium pentachloride diethyletherate, (prepared indirectly see sections 2:2, 2:5, 2:7) gave no evidence of chloride elimination under vacuum at room temperature. The presence of non-crystalline white powders, and methyl and ethyl fluorides respectively in the thermal decomposition products of $NbF_5 \cdot OMe_2$, and $NbF_5 \cdot OEt_2$ respectively shows that these reactions can take place under more extreme conditions.

Although the vibrational spectra of some dimethyl-, and perdeutero dimethyl-ether complexes of $^{10}BF_3$, and $^{11}BF_3$ have been investigated and taken to indicate that there is no coupling between vibrational modes of the acid and base parts of the molecule later studies throw some doubt on this conclusion (32) However coupling is limited (giving shifts of 15 cm^{-1} in BF_3 modes on deuteration) and no modes are split on adduct formation. This is fairly typical of behaviour of complexes.

Because some of the CH_3 rocking and deformation modes are

either accidentally degenerate, or too weak to be observed the spectra of dimethyl etherates are quite simple in appearance. Assignments of dimethyl ether bands in the I.R. spectra of NbF_5Me_2O, and TaF_5Me_2O are given in table 1:6:1 along with dimethyl ether and $^{11}BF_3 \cdot Me_2O$ [81] bands for comparison. Because the I.R. spectrum of liquid dimethyl ether has not been recorded [83] quoted frequencies are taken from the Raman spectrum of liquid Me_2O [84] whilst quoted intensities are from the gas phase I.R. spectrum. [85] Here, and elsewhere in this chapter except where otherwise stated, assignments reflect only the major characteristic of the modes involved.

Table 1:6:1

I.R. of Me_2O complexes due to Me_2O

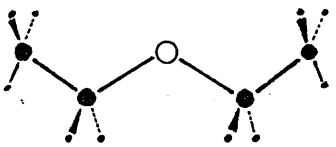
Me_2O	$^{11}BF_3 \cdot Me_2O$	$NbF_5 \cdot Me_2O$	$TaF_5 \cdot Me_2O$	
265w(I.R.)	322(R)			O(CH_3) wag
334g(R)	344(m)	314m,b		O(CH_3) rock
420w	499vw	485w	487w	COC def
610w(IR)				
918m	918w	882m,asy	870m,b	C-O sym str
		970w	885m,b	
1094s		1020m,b	1015m,b	C-Oasy str
1147s	1150m	1157m		CH_3 rock
1238(R)		1258w	1263w	CH_3 rock

* All frequencies in cm^{-1}

(R) means band is only found in raman spectra

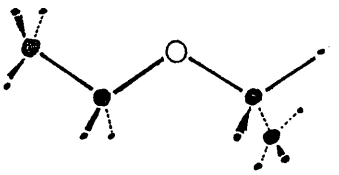
(IR) means band is only found in infra red

Vibrational spectra of diethyl ether complexes are very difficult to interpret because of the relatively large number of atoms present



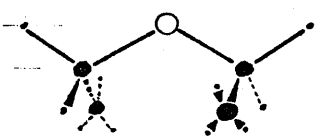
trans-trans rotamer

(tt) (C_{2v})



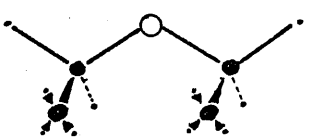
trans gauche rotamer

(tg) (C_1)



gauche-gauche rotamer

(gg) (C_2)



gauche-gauche rotamer

(gg) (C_s)

Figure 1:6:1 - rotamers of diethyl ether

• = H • = C

and rotational isomerism in the ethyl groups. There are infinite numbers of possible rotational isomers, but because rotation about carbon-carbon bonds is hindered only a few of these need be considered (see fig 1:6:1).

It has been calculated from the Kerr effect [86] that liquid diethyl ether acts as a slight modification of the (tt) rotamer with methyl groups rotated 24° from the C–O–C plane. This does not rule out an equilibrium between the various forms. Comparison of I.R. spectra of ethyl [87] and some deutero-ethyl

(88) ethers at various temperature with spectra predicted by vibrational analysis for the rotamers illustrated in fig 1:6:1 strongly suggests a temperature - dependent equilibrium between (tt) and (tg) rotamers in the free ethers. The (tt) form is the more stable by approximately one Kcal per mole and no trace of (gg) forms could be detected by I.R. spectroscopy.(87)

Use of Fieser models suggests that it is not possible for diethyl ether in the (tt) form to act as a base because of steric shielding of the oxygen atom by methyl hydrogen atoms. It is also unlikely that the tg rotamer could act as a base.

These are important conclusions because similar considerations apply to diethyl amido-, diethyl sulphide-, and diethyl selenide - compounds. Etherates are also important in certain fields of catalysis. The I.R. spectra of free, and complexed ether are compared in table 1:6:2 with a view to finding experimental evidence for these conclusions.

All the vibrational modes of each of the diethyl ether rotamers are formally both I.R. and Raman active, except the A_2 modes of the (tt) rotamer which are formally I.R. active. However models indicate that in the (tt) rotamer rotation of the methyl groups is hindered, the most stable configuration is not strictly of C_{2v} symmetry, and the A_2 modes may be weakly I.R. active.

The lists of contributions to the modes of (tg) and (tt) forms of diethyl ether (87,88) suggest, perhaps surprisingly,

Explanation of symbols used in Table 1:6:2

* Spectra and assignments of Et_2O $_{tt}$, $_{tg}$, species taken from ref.86

*, *, Principal components of modes in $_{tt}$, $_{tg}$, species

‡‡ approximate position, peak is hidden by COC stretch

‡ Symmetry of Et_2O_{tt} modes

S_o Methylene bend

T_o Methylene twist

τ Asymmetric HCH bend

W_o Methylene wag

U Symmetric HCH bend

T_o Methylene twist

P_o Methylene rock

B Methyl rock

R C-C stretch

X OCC bend

θ COC bend

M-Cl[1] Et_2O bands obscured by M-Cl bands

TABLE 1:6:2

I.R. spectra of Et_2O and Et_2O complexes *

Et_2O tt C_{2v}	‡	≠	Et_2O tg (C)	≠	Et_2O gg Calc.	Et_2O gg calc.	$TaF_5 . Et_2O$	$NbCl_5 . Et_2O$
1490m	A_1	S_o T_o	1490m	S_o To				
1473w	B_1	S_o	1484sh	S_o			1476	1474 (R)
			1466w					
1456m	A_1	∝	1456	∝				
1456m	B_1	∝	1456	∝	1446	1449	1451ms	1445 (R)
1443m	A_2	∝	1443	∝				
1443m	B_2	∝						
1414 w		W_o	1393 sh	W_o				
1383s	B_1	U, W_o	1392s	W_o, U	1339	1388	1392s	1382 (R)
1372sh	A_1	U	1372sh	U	1354	1358	1360	1366 (R)
			1372sh	U			1330m	1315w, a
1351s	B_1	U, W_o						
			1297	T_o	1291	1268	1287m	1273w
1279w	B_2	To	1279w	To				

1267(R)	A_2	To						1184s
			1183m	B, Zo	1189	1179	1193s	1070sh
1168sh	B_2	Po, B	1168	Po, B			1152d	1142m-w
1153s	A_1	B, R,	1153	S	1070	1139	998vsa	984vsa
1120vs	B	S	1097(R)	B			1092s	1084m
1077m	A_1	R	1074sh	R, B				
1043m	B_1	B, R	1023w	R	1022	1029	1020	1015sh
935w	B_1	R	916w	B, S, R			880s	871s
846w	A_1	S	837	S, B	840	900	834	823mw
822vw	B_2	B, Po	822vw	Po, B	813	808	800w	755s
794w	A_2	Po, B	794w	Po, B			778s	725sh
451vw	B_1	X	503w	Θ, X, R	530	481	512m	505m
440w	A_1	Θ, R					475w	459w
			376vw	X	284	215	350w	M-Cl

that apart from methyl and methylene rocking motions, mixing of modes has little effect on the vibrational frequencies, and it is possible to define energy regions for the vibrational motions quite closely. The calculated frequencies for (gg) and (gg^1) modes were not all given[87] (table 1:6:2), but those listed seem to define regions for the different mode types The only mode which shows a large shift between conformers is the asymmetric C-O stretch which ranges from 1153 cm^{-1} in the (tg) rotamer to 1070 cm^{-1} in the (gg) (C_2) rotamer

In the region 350-1400 cm^{-1} Et_2O(tt), Et_2O (tg) and $TaF_5 \cdot OEt_2$ all show sixteen I.R. bands (excluding metal-fluorine bands in $TaF_5 \cdot OEt_2$) and in the regions where extra bands would be expected if mixtures of conformers were present TaF_5OEt_2 shows no extra bands (for example there are two bands in the 830-950 cm^{-1} region of TaF_5OEt_2 and four in (tt)-(tg) mixtures.) It may be concluded that only one conformer of diethyl ether is present in this etherate.

In the following discussion it is assumed that $TaF_5 \cdot Et_2O$ is monomeric with site symmetry at the Ta atom being approximately C_{4v}. $TaF_5 \cdot OEt_2$ shows one I.R. band in the region 450-550 cm^{-1} and two bands in the region 1300-1380 cm^{-1} whilst Et_2O (tg) shows two and one bands in the respective regions. The medium-intensity I.R. band at 512 cm^{-1} in $TaF_5 \cdot OEt_2$ is too high and too intense to correspond to the very weak band at 451 cm^{-1} in the I.R. spectrum of Et_2O(tt). This I.R. evidence is not absolutely conclusive on its own, but when coupled with

evidence from the models it does seem certain that (tt) and (tg) rotamers of diethyl ether are not involved in complexes with pentafluorides.

The very strong bands at 998, 984, and 998 cm^{-1} in the I.R. spectra of $TaF_5 \cdot OEt_2$, $NbCl_5 \cdot CEt_2$, and $NbF_5 \cdot CEt_2$ are assigned to the asymmetric C-O stretching mode on the basis of their intensity. The shift of the asymmetric stretching mode of dimethyl ether on complexing is approximately 80 cm^{-1} (table 1:6:1). The calculated asymmetric C-O frequencies of (gg), (C_2) and (gg^1), (C_s) forms of ether are 1070 and 1139 cm^{-1} respectively. If the (gg^1) form were involved in these complexes the shift would be 140-155 cm^{-1} This is too great and the (gg) (C_2) rotamer is probably the one acting as base; I.R. and Raman spectra of $TaF_5 \cdot OEt_2$, $NbF_5 \cdot CEt_2$, and $NbCl_5 \cdot CEt_2$ suggest that all three have similar structures.

Because of lack of accurate structural data it is impossible to confirm these suggestions. I.R. Spectra of other etherates suggest that all diethyl etherates that have been investigated involve the same diethyl ether rotamer. There is no structural evidence on the angles at the oxygen atoms in diethyl etherates[89]. However complexes of $HgCl_2$ with diethyl sulphide,[90] and tetrahydrothiophen[91] have very similar angles at the sulphur atom and it is suggested that the angles at oxygen in complexes of diethyl ether, and tetrahydrofuran will be similar also. A Cr III complex of tetrahydrofuran[92] has been

found to have planar oxygen atoms and C-O bond lengths slightly longer than in free tetrahydrofuran.[93] In the absence of other data this system is taken as a model for all these ether complexes.

Sulphur and selenium are larger atoms than oxygen and the C-S-C, and C-Se-C angles are smaller in diethyl sulphides and selenides than the C-O-C angle in diethyl ether. The stabilisaton of (tt) with respect to (tg) and (gg) rotamers is thus greater in sulphides and selenides and steric shielding of the sulphur and selenium is not so great in (tt) and (tg) forms. The possibility of (tg) rotamers acting as a base increases in the series $Et_2O \rightarrow Et_2Se$ and is more favourable where there is non-planarity at the donor atom.

In complexes where alkyl sulphides act as donors the sulphur atoms are pyramidal,[90,94] and in the complexes of monodentate Et_2S studied up to 1970 (e.g. ref 90) the diethyl sulphide conformation was (gg), (C_2). The presence of (tg) donor molecules in $WF_6 \cdot (Et_2Se)_2$ would explain the apparent magnetic inequivalence of both methyl, and methylene protons in the proton N.M.R. of this compound.[32]

The published assignments of phenyl methyl ether[95] (anisole) are given in table 1:6:3. Whilst some of the assignments may be optimistic their absolute accuracy is not essential to the arguments which follow. The vibrations numbered I to IX are vibrations of the methyl group and those numbered 1 to 30 are vibrations of the aromatic ring. In anisole itself the

TABLE 1: :3

I.R. bands of free and complexed phenyl methyl ether

band	sym	OCH_3	complex	assignment	other bands in complex.
1	A'	3005vw	n.o..	C-H str	
2	A'	3095m	n.o.	C-H str	
3	A'	3062m	3060m	C-H str	
4	A'	3032*m	3020*sh	C-H str	
15	A'	3032*m	3020*sh	C-H str	
I	A'	3000ms	3029*sh	$C-H_3$ asy str	
VII	A''	2955m	2950w	$C-H_3$ asy str	
II	A')	2942	2920mw	$C-H_3$ sym str	
	)	2834	2864mw		
5	A'	1599vs	1630m	C-C str	
6	A'	1585mw	1535m	C-C str	
7	A'	1496vs	1478*vs	C-C str	
8	A'	1485sh	1490sh	C-C str	
VIII	A''	1460mw	1473*vs	$C-H_3$ asy def	
III	A'	1452mw	1459sh	$C-H_3$ asy def	
IV	A'	1390vw	1380w	$C-H_3$ sym def	
9	A'	1334m	13335w	C-C str	
10	A'	1301s		C-H def	1285mw
VI	A'	1294w‡		$C-H_3$ rock	
14	A'	1246vs	1215vs	C-O str	
11	A'	1179w	1185sh	C-H def	
12	A'	1171s	1161s	C-H def	
IX	A'	1154m		$C-H_3$ rock	1120sh
13	A'	1076s		$C-H_3$ def	1038w
V	A'	1040vs	938vs	$C-CH_3$ str.	
21	A'	1019mw	1017m	C-H def	
16	A'	994		ring mode	
22	A''	n.o.		C-H bend	
23	A''	n.o.		C-H bend	
24	A''	882s		C-H bend	
25	A''	825w		C-H bend	815s
17	A'	733s		ring mode	.786w
29	A''	754vs	-756s	C-H bend	
26	A''	690vs	(M-?)	ring mode	
27	A''	662w	(bands)	ring mode	
18	A'	615w	595w	ring mode	
19	A'	552s	490*sb	ring mode	
28	A''	508s	490*sb	C-O bend	
20	A'	264mw	300mw	C-O def	

(all frequencies in cm^{-1})

* indicates absorption assigned to more than one mode

‡ not observed in ref 8

aromatic ring probably lies in the plane of the C-O-C angle [96,97,98] but use of models indicates that the ring must be twisted out of this plane when anisole is complexed to niobium pentafluoride. The symmetry of the ring thus changes from approximately C_s, probably to approximately C_2. The band symmetries given in table 1:6:3 refer to symmetries under C_s.

The I.R. bands of NbF_5· Anisole have, where feasible, been written alongside bands in free anisole. The C-O stretching frequencies are assigned on the basis of intensities and because the consequent shifts upon coordination are compatible with those in other ethers. It can be seen that I.R. bands in free, and complexed anisole in the 770-1310 region do not correspond without assuming some shifts of up to 75 cm^{-1} or very large changes in observed intensities. That such effects are not found in complexed pyridine. (see later in this section) or substituted aromatics [99] where changes in electronic effects are much larger, suggests that changes are due to changes in symmetry of the benzene ring which change the mixing of modes.

B) Complexes with dimethyl sulphoxide

Vibrational spectre of a number of dimethyl-, and perdeutero-dimethyl-, sulphoxide complexes (e.g. $^{10}BF_3 \cdot Me_2SO$, $^{11}BF_3 \cdot Me_2SO$ [100] $Ni(ClO_4)_2$ Me_2SO [101] and a review of dimethyl sulphoxide reactions [102] have been published. When the oxygen atom of dimethyl sulphoxide is coordinated to a metal atom νS=O shifts to lower

frequencies, whilst when sulphur is coordinated a shift to higher frequencies is observed.[103,104] When dimethyl sulphoxide is oxygen-coordinated to Fe^{III} the angle Fe-O-S is 124° [105] In the absence of other data it may be assumed that the angle at oxygen is similar in other oxygen-coordinated dimethyl sulphoxide complexes. As mentioned previously (section 1:1) there are differences in properties of 1:2 complexes prepared here, and by previous workers.[11] (see table 1:6:4). In particular νS=O of $TaF_5 \cdot Me_2SO$ is surprisingly low. No other S=O frequency as low as 878 cm^{-1} has ever been reported and this might be the metal-oxygen frequency of an oxyfluoride.

Table 1:6:3

Properties of 1:2 pentafluoride: Me_2SO Complexes

Property	$NbF_5 \cdot 2Me_2SO$ ref (11)	$TaF_5 \cdot 2Me_2SO$ ref (11)	$NbF_5 \cdot 2Me_2SO$ this work	$TaF_5 \cdot 2Me_2SO$ this work
M.Pt.	44°C	63.5°C	64°C	79°C
Decomp.	70°C	95°C	54°C	79°C
νS=O	940cm^{-1}	878cm^{-1}	966,935cm^{-1}	970,930cm^{-1}

Analytical, (table 1: 9:1), spectroscopic, (figure 1:6:2, table 1:6:5), and x-ray powder photograph (figure 1:6:3, appendix 3), data all confirm that two discrete complexes of 1:1 and 1:2 stoichiometry have been prepared for each pentafluoride. The 1:1 complexes of the pentafluorides cannot be mixtures of pentafluoride and 1:2 complexes because the diethyl ether present in the pre-

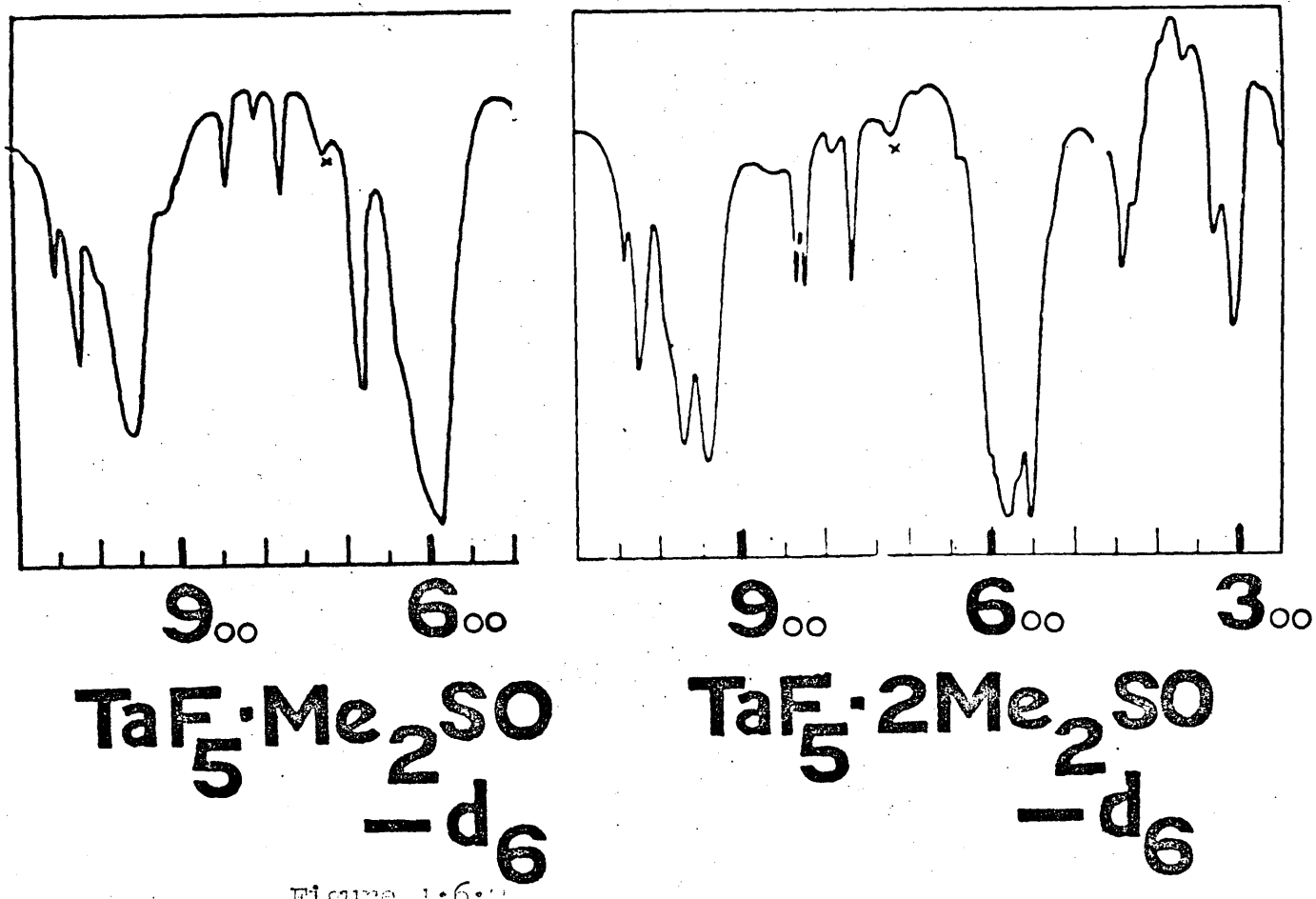


Figure 1:6:

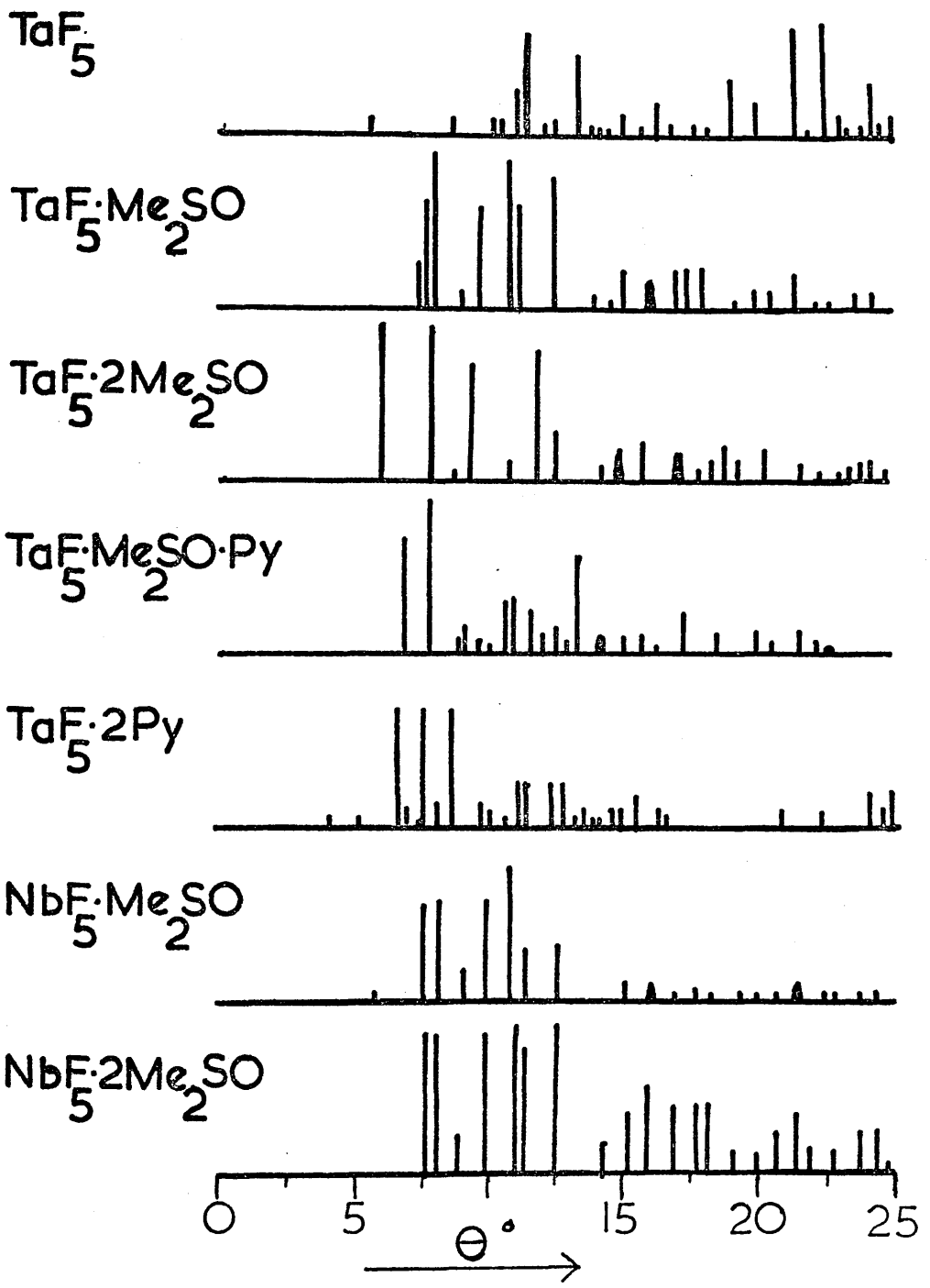


Figure 1:6:3 X-ray powder photographs of some Me_2SO complexes

Table 1:6:5

I.R. Frequencies due to Me_2SO in Me_2SO-Pentafluoride complexes.

NbF_5° DMSO	NbF_5° $(DMSO)_2$	TaF_5° DMSO	TaF_5° $(DMSO)_2$	DMSOg (107) (106)	Assignment	$DMSOd_6$ g(107) (106)	TaF_5° $(DMSO)_2d_6$	Δ(d) 1:2	Δ 1:2	TaF_5° $DMSOd_6$	Δd 1:1	Δ 1:1
3030m	3018m	3030w	3020	2973m	$\nu_1, \nu_2, \nu_{14}, \nu_{15}$, CHstr	2249	2268ms	+47	+191	2285m	+34	+57
							2258sh			2278m		
				2908m	ν_3, ν_{16}, CHstr	2124	2136mw	-	+121	2145mw	+21	-
		1426w	1440sh	1455m	ν_{17} } deg CH def, A"	1043	1027ms	-16	-15	1020sh	-23	-29
1425w	1432ms	1426w	1440sh	1440ms	ν_{18}	1025	1027ms	+2	0	1020sh	-5	-14
				1419m	ν_4 } deg CH def, A'	1025						
1418w	1419w	1418w	1419w	1405m	ν_5	1015	1022sh	+7	+14	1027ms	+12	+13
1325vw	1330w	1329mw	1331w	1319w	ν_{19}, sym, CH_3, def A"	1084sh			+8			
	1322w		1324w									
1300vw	1310vw	1302v	1308vw	1304m	ν_6, sym, CH_3, def A'	1043	1044w	+1		1046mw	+3	-2
	1304vw		1314vw									
				1287w						990shw		

955s	966s	963vs	970ms	1102s	ν_7, S=O str	1096vs	974s	-122	-132	957sb	-139	-139
	935bvs		938bs				943s	-153	-164			
1044w	1041mw	1043mw	1041m	1016m	ν_{20}, Me rock A"	803	839m	+31	+32	838m	+35	+29
	1025mw		1028m				829m					
994m	1000sh	994m	1000s	1006m	ν_8, Me rock A'	814	794w	-22	-13	801w	-12	-13
	993s		985s				789w					
992w		922w	946sh	929w	ν_{21}, Me rock A"	750	770m	+20	+17	773m	+23	-7
900w		905w		915w	ν_9, Me rock A'	756						
721mw		720mw	722m	689m	ν_{22}, asy CS str	619	642w	+23	+33	638sh	+19	+31
				672m	ν_{10}, sym CS str	611						
460s	468s	470ms	472		ν M-O		447mw			441m		
	452m		460sh		ν M-O		430sh					
358m	358m	355m	358m	376s	ν_{11}, sym CSO def	340	334mw	-6	-186	337m	-3	-21
330w	330m	330bsh	330m	335m	ν_{23}, asy CSO def	307	310s	+3	-4 1			
				333s								
	330m		310ms		ν M-F		310s					

g ≡ gas l ≡ liquid Δ ≡ shift between free and complexed DMSO

d indicates hexadeutro-DMSO

paration ensures that no free pentafluoride is present.

1:2 complexes of dimethyl-ether and sulphide [9] and acetonitrile [37] have been suggested to explain observed vapour pressure-composition curves but these are the first cases where both 1:1 and 1:2 compounds have been completely characterised.

The 1:2 compounds did not have sharp melting points and some gas evolution was observed just above the melting points. This is consistent with transformation of the 1:2 complexes to 1:1 complexes and free dimethyl sulphoxide followed by fluoride elimination in the melt. The 1:1 complexes are stable up to at least their melting points, which are 50-60°C higher than the decomposition temperature of the 1:2 complexes. This suggests that the first step in fluoride elimination does not involve uncoordinated dimethyl sulphoxide.

Assignment of I.R. bands due to dimethyl sulphoxide in the complexes with pentafluorides are given in table 1:6:5. The numbering and description of the modes is taken from references (106,107). The assignments of the degenerate C-H deformations, ν_{17}, ν_{18}, and ν_4, ν_5 must be regarded as no more than tentative Weak bands at 922 cm^{-1} in 1:1 complexes of dimethyl sulphoxide have been written opposite ν_2, but, by comparison with other complexes [100,101] ν_2 would be expected at approximately 950cm^{-1} and is probably obscurred by the strong metal-fluorine stretching bands. Frequencies in the region 450-475 cm^{-1} are assigned to metal-oxygen frequencies. Similar values have been found in the

$Ga(Me_2SO)_6^{3+}$, and $In(Me_2SO)_6^{3+}$ ions.(108)

The general similarity of shifts of dimethyl- and perdeuterodimethyl-sulphoxides on complexing to pentafluorides in both 1:1 and 1:2 complexes suggests very strongly that the constitution of modes is not greatly affected by complexing. The clear splitting of ν_{19}, ν_6, ν_7, ν_{20}, and ν_8 in the 1:2 complexes cannot be due to a lowering of the symmetry of individual dimethyl sulphoxide modes because this would not split ν_7, the S=O frequency. The large size of these splittings makes it unlikely that they are due to coupling of the modes in different dimethyl sulphoxide molecules, or to a correlation splitting. Inequivalence of complexed Me_2SO molecules is consistent with the results.

Raman spectra, apart from that of $TaF_5 \cdot (Me_2SO)_2$ were not very good because of problems with fluorescence and weak scattering.

C) Reactions and spectra of pyridines and methyl pyridines with pentafluorides.

Analytical data (table 1: 9 :1) clearly indicates the products of reaction of niobium, and tantalum, pentafluorides with pyridine (Py) and perdeuteropyridine ($Py\text{-}d_5$) to be 1:2 complexes. The isolation of only a 1:2 adduct from mixtures of NbF_5, Py, and diethyl ether is probably only an indication that $NbF_5 \cdot$ Py is soluble

Tantalum pentafluoride is shown, by the analytical data, to form 1:2 and 1:1 adducts with 4 methyl- and 2 - Methyl pyridine

respectively. Methyl groups in the 2- and 4- positions of pyridine should increase the electron density on the nitrogen atom. The formation of a 1:1 complex $TaF_5 \cdot 2Me\text{-}Py$ rather than a 1:2 complex is attributed to steric factors. Recent crystal studies on other 2-methyl pyridine complexes, e.g. $CuCl_2(2MePy)_2$ are not consistent with ~~a slight~~ significant distortion of the metal-nitrogen-carbon bond angles in the plane of the ring[109] It would be interesting to react 2-6-dimethyl pyridine with TaF_5 as this is sterically similar to the (tt) rotamer of diethyl ether discussed earlier in this section.

The results obtained from the reactions of NbF_5 with 2Me-Py, and 4 Me-Py are suggestive of some reduction of the niobium.

Crystal studies of pyridine [119 111] and methyl pyridine [119] complexes show the nitrogen to be almost planar and no significant differences are found in the bond lengths and angles of free [112] and coordinated [111] pyridine.

The adduct $NbCl_5 \cdot Py$ (prepared as in section 2:6) is stable in the absence of excess pyridine up to 125°C, at which temperature a little discolouration occurs, but extensive decomposition does not occur below the melting point of 220°C. Niobium pentachloride is partially reduced by excess pyridine at room temperature.[113] This suggests that either niobium V is greatly stablilised by complexing with pyridine, or that uncoordinated pyridine is needed for reaction to proceed.

The assignments of bands in the I.R. spectra in some of these complexes due to the coordinated pyridine, and 4-Me Pyridine groups are given in tables 1:6:6, 1:6:7. The scheme of labelling of the modes is that of Kline and Turkevich[114] as followed by Wilmhurst et al in a study of pyridine. The assignments of bands in coordinated pyridine are analogous to those of Sharp et al[116] except that a weak band at 870 cm^{-1} in complexed pyridine is attributed to ν_{10a}, or ν_{10b}. Weak bands in the I.R. spectra of pyridine - pentafluoride complexes remain unexplained. Where a comparison of band shifts, upon coordination, of pyridine and perdeuteropyridine is possible the agreement is generally good, although some differences, (e.g. in the bands attributed to ν_{9a}, and ν_3, at approximately 1218 cm^{-1}(Py) and 886 cm^{-1} ($Py-d_5$) shift by +3 and +19 respectively.) suggest that the composition of some vibrational modes change upon coordination. The assignments of I.R. bands of the 4-MePy complexes (given in table 1:6:7 alongside those of 4MePy, and $CoCl_2 \cdot 4MePy$ for comparison) are fairly straight forward, although some assignments, e.g. CH_3 rock, ν_1, and ring vibrations, are a little speculative. The ring vibrations, ν_{15} and ν_{16a}, are tentatively assigned Raman active frequencies. The strong bands at 332, and 346 cm^{-1} in $TaF_5 \cdot (4MePy)_2$ and $NbF_5 \cdot (4MePy)_2$ respectively are too strong to be ligand vibrations and are attributed to metal-fluorine modes. Bands in the I.R. spectra of $NbF_5 \cdot (4MePy)_2$ at 692, 688, 670 and 496 cm^{-1} are probably due to impurities.

TABLE 1:6:6

I.R. spectra of coordinated pyridine in TaF_5 complexes

Pyridine liq ∓	TaF_5. 2 Py	△	Pyridine -d5 liq ∓	TaF_5. 2Py-d_5	△	assignment
1923m	1930 w	+7				11+9a
	1848 w					
1583 vs	1609s	+26	1530	15		8a
1570	n.o.		1542	1539		8b
1482 s	1490m	+8	1340 w			19a
1441 vs			1302s	1329	+27	19b
1375 m			1322 m	1329 s	+7	14
	1238 w		1228m	1237 w	+12	d_5Py, 10a+11,3+16a
1218 s	1220 w	+3	886 m	905 m	+19	9a,3
1148 s	1159 w	+7		900 sh		15
1085 vw				900 sh		18b
1068 s	1070	+3	823s	840s	+17	18a

1030vs	1045m	+14	1019 m	1025 w	+13	12
			1043 w	1049 vw	+15	10a, +16b, 2X11
992	1017 }	+25	963s	982 ms	+19	1
	1015 }					
942	950w	+8				5
886 vw	870w	-16	762 m	770 w	+8	10b
886 vw	870 w	-16	690 w (R)	680 w	-16	10 a
749 m	760 s	+11	567 m			4
700 vs	690s	-10	530 vs	532 vs	+2	11
652 w	651 mw	-1	625 w			6b
605 s	635 m	+30	582s			6a
403	448 m	+47	371	410 w	+39	16b
374 vw			329 vw			16a

ǂ from ref (11 5) all frequencies in cm^{-1}

△ = shift of band on coordination

TABLE 1:6:7

I.R. spectra of coordinated 4Me-Pyridine

4-MePy liq‡	$CoCl_2$ .4-MePy*	TaF_5. $(4MePy)_2$	NbF_5. $(4\text{-}MePy)_2$	assignments
1604vs	1629	1628s	1625s	8a
	1621	1610sh	1610sh	
1566s	1560	1563	1560w	8b
1495s	1504	1511mw	1509m	19a
1340w	1336)	1340w	1339w)	2X6b or
	1328)		1305vw)	1+16a
1223s	1242)	1243ms	1240m	9a
	1227)			
1212s	1214)	1218m	1215m	13
	1205)			
1114w		1114w	1114m-w	15+4
1070m	1074)	1070s	1069ms	18a
	1071)			
1042s	1043	1031	1040m	CH_3 rock
994s	1033	1031s	1029m	1
		1012vw)	)	?
		1008vw)	1006w)	?
972m	983)	970w	969w	17a
	964)			
872w		885w)	888w)	5,10a
		868mw)	867mw)	
799vs	821	817s	819s	10b
	815			
801(R)	804	802vw	794w	12
728s	723	724m	724m	4
		704w	702w	?
			692m)	1:1 complex or
			688m)	reduced product
			670vw	
668w	669	656w	654s	6b
523m	551	530mw	555w. sh	6a
			545w, sh.	
490s	493s	506s	503ms	11
			496mw	
384(R)	375(R)	370(R) ?	375(R) ?	15
341(R)	352	350(R) ?	362(R) ?	16a
211(R)		190(R) ?		16b

‡ from ref. (117) * from ref (118)

The very weak bands in the 1000-1020 cm^{-1} region may be due to traces of oxyfluorides.

A curious feature of the spectra of pyridine, and 4-Me pyridine complexes is that the majority of bands move to higher frequencies upon coordination. This is particularly marked in pyridine complexes. There is no simple explanation for this, but one explanation is that removing a lone pair from nitrogen lessens shielding of other electrons from the nitrogen nucleus. As all the π orbitals are delocalised a drop in the energies of the orbitals associated with nitrogen would decrease energies of bonding orbitals throughout the molecule and hence all ring vibrations would be expected to rise in energy. This explanation is not, however, ideal because it would predict that the shifts of ring frequencies would be much greater than those of C-H frequencies and this is not observed.

The assignments of the I.R. spectrum of $TaF_5 \cdot 2$Me-Py are not presented here because the greater reducing power of 2Me-Py makes it unlikely that 2Me-Py complexes will be of any use in characterising mixed-ligand compounds of niobium, tantalum and molybdenum.

D) Reactions and spectra of nitriles with pentafluorides.

None of the results obtained in these reactions suggested any reduction of the metal. The reported adduct $MoF_5 \cdot (CH_3CN)_2$ [16] has an I.R. spectrum characteristic of a 1:2 adduct (see

section 1:4) and is not the same as the compound reported here. The I.R. and Raman spectra of the products of the reaction of niobium pentachloride and acetonitrile are identical to those published for $NbCl_5 \cdot CH_3CN$[119,120] after investigation by this author was complete.

The vibrational spectra of acetonitrile [121,122] monochloroacetonitrile [123] and propionitrile [124] have been extensively investigated and the assignments are given in tables 1:6:8, 1:6:9 and 1:6:10 for nitrile bands in the I.R. spectra of the complexes. The assignments are mostly straight-forward although in the region 250-450 cm^{-1} they must be regarded as tentative because bands in this region often show large shifts on coordination.

In view of the probably formation of 1:2 complexes between pentafluorides and nitriles (discussed later in this section) the bands found at approximately 2250 cm^{-1} in CH_3CN, and CH_3CH_2CN complexes are attributed to changes of phase (table 1:6:12) The I.R. of $MoF_5 \cdot CH_2ClCN$ in solution is very similar to that obtained for the 1:2 complexes (see section 1:4) and it is clear that there has been a change in coordination pattern at the metal atom. The I.R. band at 585 cm^{-1} is probably too low to be associated with MoF_6^- [63], (see section 1:4) which might be produced by self ionisation.

i.e. $2MoF_5 \cdot CH_2ClCN \longrightarrow MoF_4 \cdot (CH_2ClCN)_2^+ + MoF_6^-$

TABLE 1:6:8

I.R. of CH_3CN coordinated to pentafluorides.

CH_3CN Liq ‡	$NbF_5 \cdot CH_3CN$	$TaF_5 \cdot CH_3CN$	$MoF_5 \cdot CH_3CN$	assignments
3009s			3020m	ν_5,e, asy.C-H str.
2954			2952ms	ν_1,a_1,sym C-H str.
2291	2320ms	2327ms	2322m)	ν_3+ 4
2262	2298s	2301s	2297s)	ν_2,a_1, C≡N str
	2256w		2255w	free ligand?
1454vs	obscured by nujol			ν_3,a_1, sym. CH_3 def
1389vs	obscured by nujol			ν_7,e,CH_3 rock
1041 vs	1033m	1030mw	1028mw	ν_7,e,CH_3 rock
920 s	950m	953m	953m	ν_4, a_1, C-C str
361	410m	410m	418w	ν_8,e,CCN bend

‡ from ref. 121 (all frequencies in cm^{-1})

TABLE 1:6:9

I.R. spectra of coordinated chloro-acetonitrile.

CH_2ClCN Liq ‡	$NbF_5 \cdot CH_2ClCN$	$TaF_5 \cdot CH_2ClCN$	$MoF_5 \cdot CH_2ClCN$	assignments
3180w	3160w			$\nu_2+\nu_5(A^1)$
3021	3020m	3020m	3016ms	ν_9, a^{11}, asy. CH_2 str.
2976vs			2960vs	ν_1, a^1, sym. CH_2 str.
2347s	2320s	2324s	2312s	ν_2, a^1, C≡ N str.
1418 vs	1414m	1414m	1404s	ν_{10}, a^{11}, CH_2 twist
1277vs	1268m	1266m	1264m	ν_3, a^1, CH_2 def.
1186.m	1191w			$\nu_{11}, a^{11} CH_2$ rock
1026(R)			1620mw	ν_4, a^1, CH_2 wag
932vs	948s	950s	948s	ν_5, a^1, C-C str.
909.1w	903w	903w	893m	?
741 vs	750m	750m	752mw	ν_6, a^1, C-Cl str.
491 m	520m	521m	522m	ν_7, a^1, C-C Cl bend
359 w	387m		330w,b	ν_{12}, a^{11}, CC Cl bend
798(R)	300bw			ν_8, a^1, CCN bend

‡ From ref. 123 (all frequencies in cm^{-1})

(R) indicates Raman band.

TABLE 1:6:10

I.R. spectra of coordinated propionitrile

CH_3CH_2CN liq[‡]	CH_3CH_2CN .NbF_5	CH_3CH_2CN .TaF_5	assignments
3250w	3300vw	3303vw	ν_4+ 10 (A^1)
3085w	3155w	3160w	ν_4+ 11(A^1)
2252s	2293vs	2296s	ν_4,a^1, CN str
	2246w	2249w	free ligand ?
1461 vs	1470(R)		ν_5,a^1,ν_{16},a^1, asy CH_3 def
1431s	1418m	1415m	ν_6,a^1,CH_2 def
1316m	1306m	1305m	ν_8,a^1,CH_2 wag
1260vw	1250w	1 n.o.	ν_{17},a^{11},CH_2 twist
1075s	1073m	1075m	ν_9,a^1, asy CC str.
1004m	1000w	1000w	ν_{10},a^1, sym CH_2 rock
836w	856m	860w	ν_{11},a^1, sym CC str.
784s	783m	784m	ν_{19}, $a^{11}CH_2$ rock
754m	obscurred by		$2\nu_{20}$
670vw	M-F vibrations		ν_{21} + ν_{20}
545m	568m	570m	ν_{12},a^1,CCC bend
416w			$2\nu_{13}$
378(R)		410w	ν_{20},a^{11},CCN bend
226(R)	290b,sh	300m,b	ν_{13},a^{11}, C-CN bend
293w,gas.			ν_{21},a^{11},CH_3 torsion

‡ from ref. 123 (R) indicates a Raman frequency

section 1:4) and is not the same as the compounds reported here. The I.R. and Raman spectra of the products of the reaction of niobium pentachloride and acetonitrile are identical to those published for $NbCl_5.CH_3CN$[119,120] after investigation by this author was completed.

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In view of the probable formation of 1:2 complexes between pentafluorides and nitriles (discussed later in this section) the bands found at approximately 2250 cm^{-1} in CH_3CN and CH_3CH_2CN complexes are attributed to combination, or difference modes rather than traces of excess ligand.

It is thought that the apparently crystalline solid formed when niobium, or tantalum pentafluoride was first precipitated from acetonitrile solution might be an unstable 1:2 adduct. The changes observed in Raman spectra of mixtures of NbF_5 and CH_3CN in the metal-fluorine stretching region suggest a change in geometry about the central metal atom, but do not provide any conclusive evidence for a 1:2 adduct (table 1:6:11)

Table 1:6:11

Raman spectra of mixtures of NbF_5 and CH_3CN (all frequencies in cm^{-1}, intensities in brackets).

$NbF_5.CH_3CN$	$NbF_5.CH_3CN$ +excess CH_3CN	CH_3CN Soln of NbF_5	CH_3CN
705(90)	680(6)	706(17)	
670(w)	640(8)		
590(w)	430(w)		
	390(w)	380(30)	361w

The MoF_5-CH_2ClCN system was chosen for investigation by I.R. spectroscopy because of the high solubility of $MoF_5.CH_2ClCN$. Here the change in I.R. spectra in the region 550-760 cm^{-1} of MoF_5CH_2ClCN is too great to be due to changes of phase (table 1:6:12) The I.R. of $MoF_5.CH_2ClCN$ in solution is very similar to that obtained for the 1:2 complexes (see section 1:4) and it is clear that there has been a change in coordination pattern at the metal atoms. The I.R. bands at 585 cm^{-1} is probably too low to be associated with MoF_6^- (63)(see section 1:4) which might be produced by self ionisation.

i.e. $2MoF_5.CH_2ClCN \rightleftharpoons MoF_4.(CH_2ClCN)_2^+ + MoF_6^-$

TABLE 1:6:12

I.R. spectra of chloroacetonitrile adducts of MoF_5

Liquid CH_2ClCN	MoF_5· CH_2ClCN	band assignments	CH_2ClCN soln .MoF_5	±
2316m		impurity ?	2314sh	f,c
2265s	2312s	C≡N stretch	2305s	c
			2265mw	f
1420vs b	1404s	$A^{\prime\prime}CH_2$ twist	1414m	f
			1401s	c
730vs b	752mw	$A^{\prime}$ C-Cl stretch	736s	f,c
	710m			
	660s b			
	630 sb			
		MoF_5·2L M-F	585s asy	
494m	522m	C-C-Cl bend	520 m w	c
			495m	f

± assignment of ligand bands to either free (f) or coordinated (c) ligand

An adduct $NbCl_5 \cdot CCl_3CN$ is briefly reported in the literature [119] but it is not stated how easily it looses base. In mixtures of NbF_5 and CCl_3CN the presence of niobium pentafluoride made no difference to the volatility of CCl_3CN as judged by the time taken to pump away the latter. The trace of orange product formed on heating the mixture may be analogous to the product of reaction of WCl_5 with CCl_3CN, $(WCl_4:NCCl_2CCl_3)_2$ [125]

Summary

It has been possible to assign almost all bands due to complexed base in the I.R. spectra of pentafluoride complexes of dimethyl and diethyl ethers, anisole, dimethyl sulphoxide, some nitriles and some pyridines. The results strongly suggest that in diethyl ether complexes the base undergoes a change in configuration upon coordination and that in 1:2 complexes no uncoordinated ligand is present. Both 1:1 and 1:2 pentafluoride dimethyl sulphoxide complexes have been prepared.

1:7 Reactions between Niobium and Tantalum pentafluorides and dialkyl sulphides and selenides

These reactions have been reported to give 1:1 adducts.[9] However the only evidence is some incomplete analytical results. In later investigations of these systems no attempt was made to analyse the reaction products.[12,13] Analytical results obtained in this work were not reproduceable and did not correspond to any one compound (see table 1:9:3). N.M.R. (table 1:9:5) and N.Q.R. (section 3:3) results suggest the presence of mixtures and I.R. spectra in the metal-fluorine stretching region were not reproduceable.

I.R. spectra of diethyl sulphide itself (section 1:9, appendix 3) over a range of temperatures are explicable in terms of the presence of only one (tt) rotamer (see section 1:6 also) with some splitting of methyl and methylene-group modes in the crystalline state. Strong I.R. bands found at 450-525 cm^{-1} in samples of the pentafluoride-dialkyl sulphide adducts are tentatively assigned to a M=S mode, the M=S bond possibly being produced by the reaction $MF_5+2R_2S \longrightarrow MSF_3 \cdot R_2S+2RF$.

The bursting of tubes containing the products of reaction of NbF_5 with Et_2Se is also consistent with this reaction.

1:8 Reactions of pentafluorides with dialkylamines.

Properties of the products of reaction of niobium, and tantalum pentafluorides with diethylamine suggest the presence of more than one compound. Intensities of I.R. bands at

3300 cm^{-1} and 1650 cm^{-1} increase with time and the reaction products, at first crystalline, rapidly become slushy. The green colouration produced whilst the samples were irradiated with $CoK\alpha$ X-rays suggests decomposition and may invalidate conclusions from X-ray powder photography. No crystalline material was detectable.

The reactions of dimethylamine with NbF_5 and TaF_5 seem less complicated. $TaF_5 \cdot (NHMe_2)_2$ showed no I.R. absorptions at 1600-1650 cm^{-1} and I.R. absorptions in the range 500-700 cm^{-1} not due to the ligand are similar in pattern to those in other 1:2 adducts. $NbF_5 \cdot (NHMe_2)_2$ gave a weak I.R. absorption at 1625 cm^{-1} indicating presence of a small amount of $-NH_2$ compounds.

Both PF_5[28] and $TiCl_4$[29] initially form complexes with dialkylamines and aminolysis occurs under more extreme conditions. TaF_5, and NbF_5 give similar reactions and are also similar to PF_5 and $TiCl_4$ in that aminolysis occurs more readily with diethylamine than dimethylamine.

The very low volatility of dimethylamine solutions of niobium and tantalum pentafluoride must be due to some association between solute and solvent. There are few reports of dialkylamines having such large decreases in vapour pressure in the presence of small amounts of solute. However such depressions of vapour pressure are known for ammonia itself. Ammonium halides form a variety of compounds with ammonia.

e.g. $NH_4Cl \cdot 3NH_3$, $NH_4Br \cdot 3NH_3$, $NH_4I \cdot (NH_3)_x$ x=1,2,3,4,5,[126] some stable under 10 mm Hg of ammonia up to -5°C. Niobium pentachloride gives similar compounds with up to 18 moles of ammonia, but here the position is complicated by ammonolysis.[127]

The absorption of $1\frac{1}{2}$ moles of diethylamine per mole of MoF_5 in the reaction between the two suggests the reaction

$$2MoF_5 + 3Et_2NH \longrightarrow MoF_4 \cdot NEt_2 \cdot NHEt_2 + Et_2NH_2^+ MoF_6^-$$

However analytical data on the two isolated products does not support this (see table 1:9: 4) and some disproportionation to Mo(VI) and Mo(IV) may have occurred.

1:9 Experimental

The sources, and purification procedures for starting materials used in this chapter are described below.

Me_2O:- Air products, vacuum distilled through two traps at -78°C and kept for two months over fresh sodium.

Et_2O:- McFarlane and Smith - anhydrous grade, vacuum distilled from -60°C and kept over fresh portions of sodium until no tarnishing of the sodium surface occurred.

CH_3CN:- B.D.H. Refluxed 4 hours over 5% P_2O_5, distilled, refluxed 15 minutes over 5% fresh P_2O_5 and distilled. Kept over fresh sodium.

CH_2ClCN:- B.D.H. Fractionally distilled (B.P. 123-124°C 755 mm Hg) from P_2O_5 after refluxing 2 hours and stored over activated 4 Å molecular sieves.

CCl_3CN:- R.Emmanuel, Stored 3 months over CaH_2, fractionally distilled from P_2O_5 (B.P. 83-85°C) and stored over activated 5 Å sieve.

CH_3CH_2CN:- B.D.H. Purification as for CH_3CN.

Me_2SO:- B.D.H. Spectroscopic grade; stored over activated 4 Å molecular sieves and melted occasionally to renew contact with sieves.

Me_2SO-d_6:- Prochem Ltd, 99%, purification as for Me_2SO

Pyridine: - Analar distilled from NaOH and kept over activated 4Å molecular sieve for one week, then vacuum distilled onto

freshly activated 4 Å molecular sieve for storage.

Pyridine-d_6:- Ciba 98.5%, kept over activated 4 Å molecular sieve for one week, then vacuum distilled onto freshly activated 4 Å molecular sieve for storage.

4 Me-Pyridine:- B.D.H., fractionally distilled, (B.P. 140-142°C) twice shaken two weeks over crushed NaOH, twice vacuum distilled onto activated 5 Å molecular sieve and kept one week, stored over molecular sieve.

2Me-Pyridine, fractionally distilled (B.P. 124-126°C) and purified as 4Me-Pyridine.

$NHMe_2$:- B.D.H. Distilled through traps at -78°, twice kept one month over fresh sodium, and stored two months over sodium before use.

$NHEt_2$:- B.D.H., purification as for $NHMe_2$

Me_2S:- B.D.H., distilled under vacuum onto fresh sodium and kept two months. This was repeated twice. N.B. the residues from this purification can explode on contact with air.

Et_2S:- B.D.H. purification as for Me_2S.

Et_2Se:- Alfa Chemicals. Stored over freshly activated molecular sieve.

CH_2ClOCH_3:- B.D.H. Tech. Fractionally distilled twice, B.P. 57-60°C, kept two months over sodium and stored over 4 Å molecular sieves.

Phenyl-methyl-ether (anisole):- Hopkins and Williams, fractionally distilled (B.P. 153-4°C) and kept over sodium.

SOF_4:- donated by D.S. Ross, see D.S. Ross Ph.D. Thesis 1971

NbF_5, TaF_5, MoF_5:- see appendix I

1) Reactions between pentafluorides and nitriles

The procedure for these reactions was used for almost all the reactions reported in this chapter. Reactions were carried out in vacuum lines by condensing the bases into flasks containing the pentafluorides, allowing the mixtures to warm to room temperature, and cooling the reaction flasks with liquid nitrogen if any reaction became too violent. The pentafluorides were loaded in an inert atmosphere box, or sublimed directly into the reaction flasks. When reaction was considered complete the volatiles were pumped off, and where appropriate identified by I.R. spectroscopy.

The colourless crystals precipitated on concentration of CH_3CN, and CH_3CH_2CN. solutions of NbF_5, TaF_5 and MoF_5 broke up when kept in vacuo to give fine white powders which analysed as 1:1 complexes (see table 1:9:1). The Raman spectra of $NbF_5 \cdot CH_3CN$, and $NbF_5 \cdot CH_3CN$ in excess CH_3CN were significantly different (see table 1:6:11).

NbF_5, TaF_5 and MoF_5, all gave 1:1 complexes with CH_2ClCN. NbF_5 did not visibly interact with CH_3CN at room temperature and Raman spectra of NbF_5, and NbF_5 and CCl_3CN, were similar in the range 200-100 cm^{-1}. When the mixture of NbF_5 and CCl_3CN was heated to 60°C the NbF_5 dissolved but on later evaporation

TABLE 1:9:1

compound		ANALYSIS C	H	N	F	other elements	char temp M.Pt.°C	Physical Properties
$TaF_5.CH_3CN$	found	7.3	1.4	4.3	30.4		chars 210	white*crystalline powder
	calc	7.6	1.0	4.4	30.0		m. 236	not volatile 200°C
$TaF_5.CH_2ClCN$	found	6.5	1.5	3.6	27.2	Cl=9.5	chars 140	colourless crystals
	calc	6.8	0.6	4.0	27.0	Cl=10.1	m.74.5	volutile 10^{-4}mm, 20°C
$TaF_5.CH_3CH_2CN$	found	10.4	2.2	3.9	28.9		chars 155	white crystalline powder
	calc	10.9	1.5	4.2	28.7		m. 166	not volatile 100°C
$NbF_5.CH_3CN$	found	10.4	1.3	6.0	41.0			white*cyrstalline
	calc	10.5	1.3	6.1	41.5			powder
$NbF_5.CH_2CLCn$	found	8.5	1.1	4.8	36.1	Cl=12.5	m. 65	colourless crystalo
	calc	9.1	0.8	5.3	36.1	Cl=13.5		volatile 10^{-3} mm, 20°C
$NbF_5.CH_3CH_2CN$	found	14.7	2.3	5.7	38.7			white crystalline powder
	calc	14.8	2.1	5.8	39.1			not volatile 100°C
$MoF_5.CH_3CN$	found	10.5	1.4	5.9	39.7		chars 190	white powder
	calc	10.4	1.3	6.0	40.9		m. 176	
$MoF_5.CH_2ClCN$	found	9.3	0.9	5.4	34.5	Cl=13.6	m.59.5	colourless crystals
	calc	9.0	0.8	5.3	35.6	Cl=13.3		volatile 10^{-4},20°C
$TaF_5.OEt_2$	found	13.6	2.7		26.8			colourless liquid*
	calc	13.7	2.9		27.1			
$TaF_5.OMe_2$	found	7.4	1.9		29.5			colourless crystals
	calc	7.2	1.9		24.2			volatile 10^{-3}mm.20°C

$NbF_5.OEt_2$	found	18.2	3.8		36.4.			colourless liquid*
	calc	18.3	3.8		36.3			
$NbF_5.OMe_2$	found	10.3	2.3		40.4		chars 150	colourless crystals
	calc	10.3	2.6		40.6		m. 34	volatile 10^{-3}mm, 20°C
$NbF_5.OMeC_6H_5$	found	27.7	2.9		30.5	Nb=13.9		viscous orange-red
	calc	27.5	2.6		31.0	Nb=13.4		liquid
$TaF_5.(Me_2SO)_2$	found	11.0	2.9		22.0	S=14.7	m.79 lost	white crystalline powder
	calc	11.1	2.8		22.0	S=14.8	gas 110	not volatile 80°C
$TaF_5.Me_2SO$	found	6.8	1.8		27.0	S=9.0	m 133 no	white crystalline powder
	calc	6.8	1.7		26.8	S=9.1	decomp 133	volatile 100°C
$TaF_5.(Me_2SO)_2$[d]	found	10.8	5.6		20.6	S=14.4		white crystalline powder
	calc	10.8	5.4		21.4	S=14.4		not volutile 20°C
$TaF_5.Me_2SO-d_6$	found	6.3	3.3		23.3	S=8.3	m131	white crystalline powder
	calc	6.7	3.3		26.4	S=8.9		volatile 100°C
$NbF_5.(Me_2SO)_2$	found	14.1	3.7		27.2	S=17.8	m 55-64	white crystalline powder
	calc	14.0	3.5		27.6	S=18.6		non volatile 60°C
$NbF_5.Me_2SO$	found	9.1	2.4		35.2	S=12.1	m.125 some	white crystalline powder
	calc	9.0	2.3		35.7	S=12.1	gases lost	volatile 100°C
$TaF_5.Py_2$	found	27.4	1.9	6.4	22.2		chars 180	white crystalline powder
	calc	27.7	2.3	6.5	21.9		-250 m 170	not volatile 150°C
$TaF_5.(Py\text{-}d_5)_2$	found	26.2	4.5	6.1	21.3		chars 180	white powder not
	calc	26.2	4.5	6.3	21.4		m 160	volatile 150°C

$NbF_5.(Py\text{-}d_5)_2$	found	31.2	5.6	7.3	25.1		white crystalline powder
	calc	33.7	5.6	7.9	26.7		not volatile 150°C
$TaF_5.(4\ Me\text{-}Py)_2$	found	29.5	3.0	6.2	20.7		white crystalline powder
	found	28.6	3.1	6.1	20.8		not volatile
	calc	31.1	3.0	6.1	20.5		
"$NbF_5.(4M_2\text{-}Py)$"$_2$	found	35.5	3.2	6.3	29.0	chars 120	fawn coloured powder
$NbF_5.(4Me\text{-}Py)_2$	calc	38.5	3.8	7.5	25.4	m 161	
$NbF_5.4Me\text{-}Py$	calc	25.6	2.5	5.0	33.8		
$TaF_5.2Me\text{-}Py$	found	20.12	2.1	3.9	25.0		white powder
	calc	19.5	1.9	3.8	25.7		

* indicates that physical properties differ from those previously reported

of the mixture at room temperature all the chloroacetonitrile was removed and only a trace of orange powder was present in addition to the original NbF_5

2) Reaction of niobium and tantalum pentafluorides with ethers

At room temperature the reactions of NbF_5 or TaF_5 with Me_2O, or Et_2O all produced 1:1 complexes as the only involatile products. $NbF_5 \cdot OEt_2$, and $TaF_5 \cdot OEt_2$ were miscible in all proportions with diethyl ether and mixtures with ether gave only one set of ethyl-group signals in their N.M.R. spectra. When $NbF_5 \cdot OMe_2$, or $NbF_5 \cdot OEt_2$ were heated to 140°C for ten hours in a stainless steel bomb the gaseous products contained methyl, or ethyl fluoride respectively. The residues were messy, water sensitive, white-blue powders.

Niobium pentafluoride is quite soluble in anisole (phenyl-methyl ether) at room temperature. Although at 40°C a reaction occured to give a 1:1 complex, almost all the anisole could be pumped from a fresh solution of niobium pentafluoride at room temperature. At room temperature chlorodimethyl ether gave a black tar when reacted with niobium pentafluoride.

3) Reactions of niobium and tantalum pentafluorides with dimethyl sulphoxide.

Dimethyl sulphoxide is involatile and does not readily distil even under high vacuum. It was loaded in the inert atmosphere box into one side of a double-sided flask (see appendix I)

containing pentafluoride in the other side, and tipped onto the pentafluoride after the flask had been evacuated. In later experiments dimethyl sulphoxide was reacted with pentafluorides in diethyl ether to dissipate the heat of reaction and prevent breakdown of the dimethyl sulphoxide. Quantities of reactants used in typical preparations are given in table 1:9:2. When reaction was complete the products were washed several times with ether to remove excess reactants and vacuum dried.

Table 1:9:2

Reactants used in preparation of dimethyl sulphoxide complexes (quantities in m. moles XS ≡ excess, i.e. > MF_5)

Compound	pentafluoride	Et_2O	Me_2SO
$TaF_5 \cdot Me_2SO$	7.24	XS	4.76
$TaF_5 \cdot (Me_2SO)_2$	10.77	XS	21.45
$TaF_5 \cdot Me_2SO\text{-}d_6$	3.21	4.21	2.73
$NbF_5 \cdot Me_2SO$	4.84	4.54	4.20
$NbF_5 \cdot (Me_2SO)_2$	9.19	XS	22.5

When dimethyl sulphoxide was added directly to NbF_5 a vigorous, exothermic reaction took place and the products were a white, crystalline solid, a viscous, colourless liquid, and a gaseous mixture. The gaseous products gave peaks in the mass spectrum at mass numbers 104(s), 94(mw), 87(s), 86(s), 85(vs),

77(ms), 76(ms), 69(ms), 66(m), 57(m), 47(m), 33(m) and 17(s) and an I.R. spectrum with peaks at 2940vs, 2860vs, 2820vs, (1740, 1747, 1718), P.Q.R. s, 1501 m, 144vs,b, (1323, 1314, 1300) P.Q.R. 1035vs, 1018 vs, 960s, 700m, 680m. It is not possible to identify the gaseous products from this data.

When the reactions were repeated using diethyl ether as a solvent it was found that the composition of the precipitates formed on addition of dimethyl sulphoxide varied when the ratio of MF_5:Me_2SO was less than 1:1, or more than 1:2 adducts precipitated were of 1:1 or 1:2 stoichiometry respectively. When the ratio was between 1:1 and 1:2 I.R. spectra, and x-ray powder photographs indicated the presence of a mixture of 1:1 and 1:2 adducts with no evidence for any other phases. When the ratio of Me_2SO: MF_5 was greater than 4:1 no precipitate was formed and the products separated into two fluid layers.

4) The reaction between $TaF_5 \cdot Me_2SO$ and pyridine.

The product of quantitative addition of pyridine to an equimolar amount of $TaF_5 \cdot Me_2SO$ suspended in diethyl ether was a white powder with an x-ray powder photograph which was not a superposition of NbF_5:Me_2SO on that of $NbF_5 \cdot 2Py$ (see fig 1:6)

5) Reactions between pentafluorides and pyridines.

These reactions gave $MF_5 \cdot 2Py$ (M=Nb,Ta,Mo) as white crystalline powders. $NbF_5 \cdot 2Py$ and $TaF_5 \cdot 2Py$ were almost insoluble in diethyl ether but moderately soluble in mixtures of $MF_5 \cdot OEt_2$

and diethyl ether . Despite changes in the ratio of reactants only products with 1:2 stoichiometry could be obtained from reactions of NbF_5, or TaF_5 with pyridine in ether. Dr. A.F. Cameron has made some preliminary single crystal studies on crystals of $MF_5 \cdot 2Py$ obtained from the $MF_5 \cdot OEt_2$, OEt_2, Py mixtures. These show $NbF_5 \cdot 2Py$ and $TaF_5 \cdot 2Py$ to be isostructural, with the monoclinic crystal type $P2_1$ or $P2_{1/m}$ The known cell dimensions of $NbF_5 \cdot 2Py$ are a=7.72Å, b=14.85Å, c=14.88Å, (all ± 0.15Å) $\beta \simeq 90°$

Tantalum pentafluoride reacted with 2- and 4- methyl pyridines to give compounds of 1:1 and 1:2 stoichiometry respectively(see table 1:9:1) NbF_5 reacted, in about five minutes at room temperature, with 2Me-Py to give an inhomogeneous mixture of grey and white solids.

6) Reactions of niobium and tantalum pentahalides with dialkyl-sulphides and -selenides

The products of reaction of NbF_5 and TaF_5 with dialkyl sulphides did not give analytical results (listed in table 1:9:3) consistent with the presence of single compounds. The diethyl sulphide reactions gave viscous yellow liquids whilst dimethyl sulphide and NbF_5 or TaF_5 gave white solids slightly volatile in vacuo at 20°C. NbF_5 and Me_2S also yielded traces of involatile blue solids.

Niobium pentachloride reacted with dimethyl sulphide to give a brown solid in the presence of excess dimethyl sulphide. When

Table 1:9:3.

Analytical data for reactions with dialkyl sulphides

Compound/		ANALYSIS				
reaction		C	H	N	F	Cl
NbF_5+Me_2S	Found	9.3	2.6	15.2	31.3	
NbF_5+Me_2S	found	9.9	2.6	13.3	36.4	
NbF_5+Me_2S	found	9.3	2.6	12.7	36.0	
$NbF_5.SMe_2$	calc	9.6	2.4	12.8	38.0	
$NbSF_3.SMe_2$	calc	9.8	2.5	26.3	23.5	
$NbF_4.SMe_2$	calc	10.4	2.6	13.9	32.9	
$NbCl_5$+Me_2S	found	7.4	11.9	9.7		47.2
$NbCl_5.SMe_2$	calc	9.7	1.8	9.7		53.3
TaF_5+Me_2S	found	6.7	1.8	9.3	31.4	
TaF_5+ Me_2S	found	6.9	4.7	8.8	26.2) 25.9)	
$TaF_5.SMe_2$	calc	7.1	1.8	9.5	28.1	
$TaSF_3.SMe_2$	calc	7.2	1.8	19.3	17.2	
$TaF_4.SMe_2$	calc	7.5	1.9	10.1	23.8	
NbF_5+Et_2S	found	15.7	3.2	10.3	31.8	
NbF_5+Et_2S	found	14.8	3.6	9.7	34.1	
$NbF_5.SEt_2$	calc	17.3	3.6	9.7	34.2	
TaF_5+Et_2S	found	11.8	2.4	7.8	23.4	
TaF_5+Et_2S	found	11.6	3.3	7.8	24.0	
$TaF_5.SEt_2$	calc	13.1	2.8	8.8	26.0	

the excess dimethyl sulphide was removed a bright orange powder formed.

Niobium pentafluoride reacted with diethyl selenide to give a viscous red liquid which darkened in colour over a period of several days. If kept too long at room temperature the sample tubes containing the liquid exploded, so the compound was not further investigated.

7) Reactions of pentafluorides with dialkylamines.

On allowing mixtures of dimethylamine and NbF_5, or TaF_5 to warm from -196°C a reaction started at about -20°C to give yellow, or white solids respectively. The colours of the solids dissolved in excess amine were the same as those of the isolated solids. However even at mole ratios of pentafluoride : dimethylamine of 1:6 the vapour pressure of the solutions at room temperature was only a few millimeters. Dimethylamine boils at 7.4°C. The stoichiometry of the products left after pumping on the niobium solution for four days corresponded to 1:2 adducts (see table 1:9:4). The complexes of niobium and tantalum pentafluorides did not visibly change in appearance over quite large periods of time.

It was also difficult to remove excess diethylamine from the yellow products of its reaction with niobium and tantalum pentafluorides. Reaction of niobium pentafluoride with diethylamine gave a yellow slush. "$TaF_5 \cdot (NHEt_2)_2$" became slushy within a few weeks. All the amine compounds exhibited fluorescence in the Raman spectra although it was possible to obtain Raman spectra

TABLE 1:9:4

Analytical data for reactions with dialkyl amines

Compound/ reaction		ANALYSIS C	H	N	F	Nb/MO
NbF_5+$NHMe_2$	found	17.1	5.4	9.9	34.4	Nb=33.9
$NbF_5 \cdot 2NHMe_2$	calc	17.3	5.1	10.1	34.2	Nb=33.4
TaF_5+$NHMe_2$	found	13.0	3.8	7.5	26.3	
$TaF_5 \cdot 2NHMe_2$	calc	13.1	3.9	7.7	26.0	
NbF_5+$NHMe_2$	not analysed		obvious	mixture		
TaF_5+$NHEt_2$	found	18.1	3.8	6.9	24.2	
$TaF_5 \cdot 2NHEt_2$	calc	22.8	5.3	6.6	22.5	
MoF_5+$NHEt_2$						
brown product	found	35.1	8.1	10.1	22.9	
white product	found	30.0	7.5	9.4	26.1	Mo=28.2
$MoF_4 \cdot NEt_2 \cdot NHEt_2$	calc	30.3	6.7	8.9	23.9	Mo=30.2
NH_2ET_2F	calc	51.7	13.0	15.0	24.4	Mo=0.0
$NH_2Et_2MoF_6$	calc	16.9	4.3	4.9	40.1	Mo=33.8
$MoF_4 \cdot NEt_2$	calc	30.6	6.4	8.8	24.0	Mo=30.3

of the methylamine adducts.

When a mixture of molybdenum pentafluoride and diethylamine was allowed to warm to room temperature the products of reaction, which could only be partially separated by washing with amine were a brown compound, sparingly soluble in amine, and a nearly white powder moderately soluble in excess amine. The observed gain in weight corresponded to a mole ratio MoF_5:$NHEt_2$ of 2:3 in the involatile products.

I.R. and Raman spectroscopic measurements were carried out as described in Appendix I. Reaction of samples with KBr plates used for infra-red analysis was detected by appearance of a red-brown colour in the sample, or the appearance of a very strong absorption in the I.R. spectra at approximately 600 cm^{-1} All of the 1:1 complexes, but none of the 1:2 complexes, were observed to react with K Br. Reaction with AgCl Plates, detected by appearance of a red colouration in the sample was observed with the products of reaction of pentafluorides with dialkyl sulphides.

When nujol was heated with niobium pentafluoride to 130° for six hours no new peaks in the I.R. spectrum of the nujol were detected in the range 1000-1200 cm^{-1}. No gaseous products were found and the I.R. spectrum of the niobium pentafluoride was unchanged.

N.M.R. measurements were carried out on samples loaded into tubes, degassed at 400°C in vacuo, in the inert atmosphere box and sealed under vacuum. The results are given in table 1:9:5 Mass spectra were run on the M.S.12 mass spectrometer under

TABLE 1:9:5

^{19}F and ^{1}H NMR spectral results

COMPOUND	T°C	^{19}F*	τ ^{1}H		J_{HH}
			CH_3	CH_2	Hz
$NbF_5 \cdot OEt_2$	33	-156	8.57	5.62	5
OEt_2	33		8.84	6.57	5
$NbF_5 \cdot ONeC_6H_5$	10-80	n.o.	7.32		
$NbF_5 \cdot CH_2ClCN$	90	-161		6.85 5.93	
$NbF_5 \cdot SeEt_2$	55 10-40	n.o.	8.5	6.9	v.b.
"$NbF_5 \cdot SMe_2$"	33 33	-147	7.59 8.00		
"$NbF_5 \cdot SEt_2$" sample(1);	100 90 75 60 50 40 30 10 0 -20	-155.4 -154.3 -151.8 -148.8 -146.6 -143.6 -130.0	 8.79 8.79 8.79 8.76 8.75 8.76 8.77	 7.30 7.29 7.29 7.28 7.29 7.28 7.28	 7.6 7.6 7.7 7.8 7.6 7.4 b
"$NbF_5 \cdot SEt_2$"(2)	33	-150.3	8.63	7.02	7.4
" sample(3)	33	-158.8	8.60	6.92	
" sample(4)	33	-157.6			
SEt_2	33		8.82	7.53	7.1
$NbF_5 \cdot (SEt_2)_{1.6}$	33	-141.5	8.60	6.90	
$NbF_5 \cdot (SEt_2)_{1.9}$	33	-144.1	8.69	7.21	
$NbF_5 \cdot (SEt_2)_{4.5}$	33	-146.4	8.73	7.37	
$NbF_5 \cdot (SEt_2)_{5.6}$	33	-147.6	8.75	7.39	
$NbF_5 \cdot (SEt_2)_{6.2}$	33		8.75	7.40	
$NbF_5 \cdot (SEt_2)_{6.4}$	33	-148			
$NbF_5 \cdot (SEt_2)_{10.4}$			8.90	7.44	

/cont.

$TaF_5 \cdot CH_2ClCN$	100 85 95 10	-93 -93 -92 -92			
"$TaF_5 \cdot SEt_2$"(1) " sample (2)	33 40 25 10 -10- -45	-88 -82.7 -78 -80vb n.o.	8.77 8.57 8.56 8.51 8.58	7.06 6.88 6.92 6.91 6.90	— — — — —

* ^{19}F are given in ppm from CCl_3F, the -ve sign indicates that all ^{19}F resonances are downfield from CCl_3F.

NbF_5 gave one broad ^{19}F resonance ^{19}F=-184 ppm at 80-100°C
TaF_5 gave me broad resonance at -104 ppm at 100-120°C
A mixture of NbF_5 and TaF_5 with mole ratio 1:0.57 gave the a resonace at -151 ppm at 80-100°C, linewidths 80°-230Hs, 100°160Hz, 110°150Hz 120° 130Hz.

conditions as described for niobium pentafluoride in section 1:3. X-ray powder photographs were run in quartz, or pyrex tubes of 0·5, or 0·3 mm diameter with a 114·6 mm Debye-Scherrer camera using Co-Kα irradiation. Tubes were loaded in the inert atmosphere box and sealed with a flame, and a small amount of Kel-F wax.

Temperature dependent I.R. studies of diethyl sulphide were attempted, using the cell described in Appendix 1, to investigate rotational isomerism in diethyl sulphide. No I.R. bands disappeared on cooling but splitting of several bands was observed when samples were annealed for a few minutes at approximately -120°C before cooling to -196°C. No splittings were observed when diethyl sulphide was cooled directly to -196°C (full lists of bands observed are given in appendix 3)

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CHAPTER II

Substitution Reactions of Pentafluorides.

2:1 Introduction

This chapter deals principally with some attempted preparations of fluoride-halides and fluoride - pseudohalides of niobium and tantalum. MF_5, MCl_5, MBr_5, MI_5[1], $M(OR)_5$ (R=Me,Et,^nPr),[2,3] $M(NCS)_5$[4-7] and $M(NMe_2)_5$[8] (M=Nb,Ta) are all known and although $M(CN)_5$, and $M(NCO)_5$ have not been prepared some chloride-cyanides [9] and chloride cyanates [7] are known. A number of mixed halides and mixed halide-pseudohalides of Nb, and Ta are known but until this work was started the only Nb or Ta mixed "halides" containing fluorine were the tetrachloride-fluorides,[10,11] and fluoride-alkoxides.[12]

Many oxidation, and substitution methods are available for preparation of halides and a classification of some of these is given below

(1) Oxidation

(a) of metals by halogens

e.g. $2Nb+5F_2 \xrightarrow{150^\circ} 2NbF_5$ (see appendix 1)

(b) of metals by reactive halides

e.g. $3Nb + 8BrF_3 \longrightarrow 3BrF_2.NbF_6 + 5/2Br_2$

$BrF_2.NbF_6 \longrightarrow BrF_3 + NbF_5$ [13]

Method 1b seldom gives pure products because the salts (e.g. $BrF_2.NbF_6$) are quite stable.

(c) of lower halides: The lower halides of niobium

and tantalum have not been well characterised. Use of method 1 c has not been reported in niobium, or tantalum chemistry, but oxidation of lower halides has been successfully used in non-metal pentahalide chemistry

e.g. $PF_3+Cl_2 \rightarrow PCl_2F_3$ (14)

The frequent need for high temperatures to initiate oxidation reactions has tended to limit their use in halide preparations for pseudo-halogens, and halides, often decompose at moderately high temperatures.

2) Substitution. The generalised reaction is $MX_5+ZM'Y_x \rightarrow MX_{5-zx}Y_{zx}+ZM'X_x$ The degree of substitution which can be achieved is often limited by the nature of M' and Y. The reactions may be classified by the nature of M'.

a) M'=H. These reactions have been much used to produce ethoxides (2,3) cyanides, (9) and alkylamides and dialkylamides (15,16,17,18)

e.g. $TaCl_5+3EtOH \rightarrow Ta\ Cl_2(OEt)_3+3HCl$

$TaCl_5+5\ EtOH+5NH_3 \rightarrow Ta(OEt)_5+5NH_4Cl$ (2)

b) M'= alkali metal. These reactions have been used extensively for preparation of metal pseudohalides using CH_3CN as a solvent.

e.g. $NbCl_5+5LiNMe_2 \rightarrow Nb(NMe_2)_5+5LiCl$ (8)

c) M'=As. AsF_3 has been used to produce the tetrachloride-fluorides of niobium and tantalum (10,11) and represents one of the few reported cases where a halogen attached to niobium, or tantalum is replaced by a more electronegative halogen in a

substitution reaction.

e.g. $3PCl_5.NbCl_5+6AsF_3 \longrightarrow 3PF_5+3NbCl_4F+6AsCl_3$

d) M^1=Nb,Ta. These reactions have not been attempted.

e) M^1=Si. The use of Me_3Si halides and pseudohalides in substitution reactions with tungsten and boron halides is well established (e.g. references 22,23). They have not, however, previously been used for preparation of Nb, or Ta mixed halides. The reactions are thought to proceed via intermediate acid-base complexes which can, in some cases, be isolated

e.g. $Me_3SiCN+BF_3 \longrightarrow Me_3SiCN.BF_3 \longrightarrow Me_3SiF+BF_2CN$ (22).

This mechanism is not proved, however, because the complex may dissociate before substitution occurs. The strong Lewis acidity of Nb and Ta (V) makes it possible that it may, in some cases, be difficult to remove excess reagent (Me_3SiX). Me_3Si compounds are generally less reactive as substituting agents than alkali metal salts (24,25,4-8) which can replace all the halogens of transition metal halides with pseudohalogens.

f) M^1= other elements. Few other halides have been used as substituting agents, but it is suggested that phosphorus, germanium, and sulphur compounds may, at some stage, be found useful because the by-products of reaction should, as in the Me_3Si-X reactions, be volatile and easily removed from the reaction mixtures.

A list of [illegible], pentavalent halides, mixedhalides, mixed pseudohalides, and pseudo-halides of Nb, and Ta is

Table 2:1:1 Nb and Ta (V) Halides

Compound	Preparations	Reagents	Ref	Comments
MF_5	1a,b	$M+F_2$, BrF_3.	27,13	F-bridged tetramer
MF_5	2f	MCl_5+ZnF_2	28	
MCl_5, MBr_5, MI_5	1a	$M+Br_2$, Cl_2, I_2	29,30	X-bridged dimers (not iodides)
MCl_5	2e	MF_5+TiCl_4	26	
MCl_4F	2c	MCl_5+AsF_3	10,11	F-bridged tetramer
$M(CNS)_5$	2b	MCl_5+KCNS	4-7	contains NCS bidentate bridges
$MCl_x(CNS)_{5-x}$ X=0-4	2b	MCl_5+KCNS	4-7	CNS is N bonded
$MCl_x(CNO)_{5-x}$ x=0-4	2b	MCl_5+KCNO	7	NCO is N bonded to metal
MX_4CN X=Cl,Br	2a	MX_5+HCN	9	CN is C bonded to metal.
$M(NR_2)_5$	2b	MCl_5+LiNR_2	8	$NR_2=NMe_2$, NC_4H_8
$MCl_3(NR_2)_2.NHR_2$ R=H,Me,Et	2a	MCl_5+NHR_2	15-18	
$MX_x(OR)_{5-x}$ X=Cl,F,R=Me,Et X=0-4	2a	MX_5+ROH	2,3 32	$M(OR)_5$ compounds are O-bridged dimers(3,19)

given in table 2:1:1 together with notes on the methods used in their preparation(labelled as above).

In all reactions producing mixed halides analytical data are not sufficient proof that only one compound is present in the reaction products. For instance $NbF_4.NEt_2$ would give the same analysis as an equimolar mixture of $NbF_3.(NEt_2)_2$ and NbF_5. Reactions should, ideally, be done in solution to ensure homogeneous reaction products, but this is difficult because no suitable non-interacting solvent has been found for transition metal pentafluorides. C_6H_6, and C_6F_6 are poor solvents for pentafluorides. Lewis bases have been used as solvents (see Chapter 1) but in these solutions pentafluoride complexes and not pentafluorides are present.

In recent experiments the monosubstituted anions MX_5Y^- (X, Y=Cl, Br, 1) were produced by addition of Et_4NY in 1:1 stoichiometry to CH_3CN solutions of MX_5.[33] The anions $MCl_xF_{6-x}^-$ (X=0 to 5) have been observed by ^{19}F N.M.R. spectroscopy of solutions of $NbCl_5$, or $TaCl_5$ in 60% HF[31] but MF_5Cl anions have been reported to undergo dismutation when attempts were made to isolate them in solid state.[21] (In this chapter the word dismutation will be used to indicate a reaction in which a mixed halide reacts to give species with different halogen ratios

e.g. $2MCl_3F_2 \longrightarrow MCl_4F + MCl_2F_3$

A material will be said to be dismutated when the species present

do not all have the same composition as the bulk). There is also N.M.R. evidence for non-ionic chloride-fluorides, in melts and solutions, of Nb(V)[20], Ta(V)[20] and W (VI)[34] other than those which have been isolated pure ($NbCl_4F$, $TaCl_4F$, $WClF_5$). In all cases where reactions are carried out in solution it must not be assumed that the species precipitated by concentration of the solutions are the ones thermodynamically most stable to dismutation in solution.

Reactions reported in this chapter produced mixed "halides" and 1:1 and 1:2 complexes of mixed "halides" with bases. Where dismutation and scrambling reactions are feasible there is no reason to assume that the ratios of F:X(X=another halogen or pseudo-halogen) in compounds separable from mixtures will be the same for all systems. The 1:1 complexes may show greater similarities to the mixed hexahalide anions than to mixed pentahalides due to the greater inequivalence of chemical bonds in the latter. It may be predicted that the stable ratios of F:X will not be the same for all X. Where X is very bulky the interactions between X groups should increase rapidly as the degree of substitution increases and these compounds may show greater stability to dismutation reaction although reductions may become more favourable.

e.g. $MX_3Z_2 \longrightarrow MX_3+Z_2$

Most Nb, and Ta pentahalides and pseudohalides appear to be polymeric in the solid state containing bridging

"halogen" atoms. The penta-dialkylamides are notable exceptions.[35] Here steric strain, to which the instability of $M(NEt_2)_5$, (M=Nb,Ta), has been attributed, may be an important factor, or M-NR_2-M bridges may be inherently unstable. The intense colours of dialkyl amino compounds and the planarity of nitrogen atoms in $W(NMe_2)_6$[36] suggest $N_{p_\pi} \longrightarrow M_{d_\pi}$ bonding and the possibility of nitrogen-metal charge transfer.

There are spectroscopic criteria for deciding whether the CN, or CNS and CNO compounds of low oxidation state are C,N,S, or O bonded. However the last general survey of the spectra of cyanates and thiocyanates is now outdated by more recent publications containing information on systems with metal in high oxidation states (see e.g. ref 43,44). It is beyond the scope of this thesis to extend the correlations to the more recent data.

2:2 General Considerations

To illustrate the problems of identifying solid, mixed halides, six possible "forms" of a hypothetical material, analysing as MX_3Z, and consisting of square-planar molecules, shown in figures 2:2:1 a-f, will be considered.

In situation "a" there are two distinct compounds, MX_4 and MX_2Z_2. This situation is readily detected when MX_4, and MX_2Z_2 are not isomorphous, for x-ray powder photographs, and vibrational spectra, consist of the superimposed photographs, and the spectra of MX_4, and MX_2Z_2, and in theory the I.R; and Raman bands should not be broader than in the isolated compound.

In situation "b" substitution is non-random but dismutated, for no MX_3Z molecules are present. X-ray powder photographs will show only one crystalline substance, but this may exhibit some disorder effects, and the material will not necessarily be isomorphous with either MX_4, or MX_2Z_2. I.R. and Raman spectra may not consist of the superimposed spectra of MX_2Z_2 and MX_4. The observed bands may be broader, and some extra bands may arise because of the lower symmetry of the lattice sites.

Figure c represents a situation where MX_4, and MX_2Z_2 are not necessarily isomorphous but are partially soluble in each other. Substitution is non-random, but dismutation has occurred. This situation can be very difficult to recognise for two

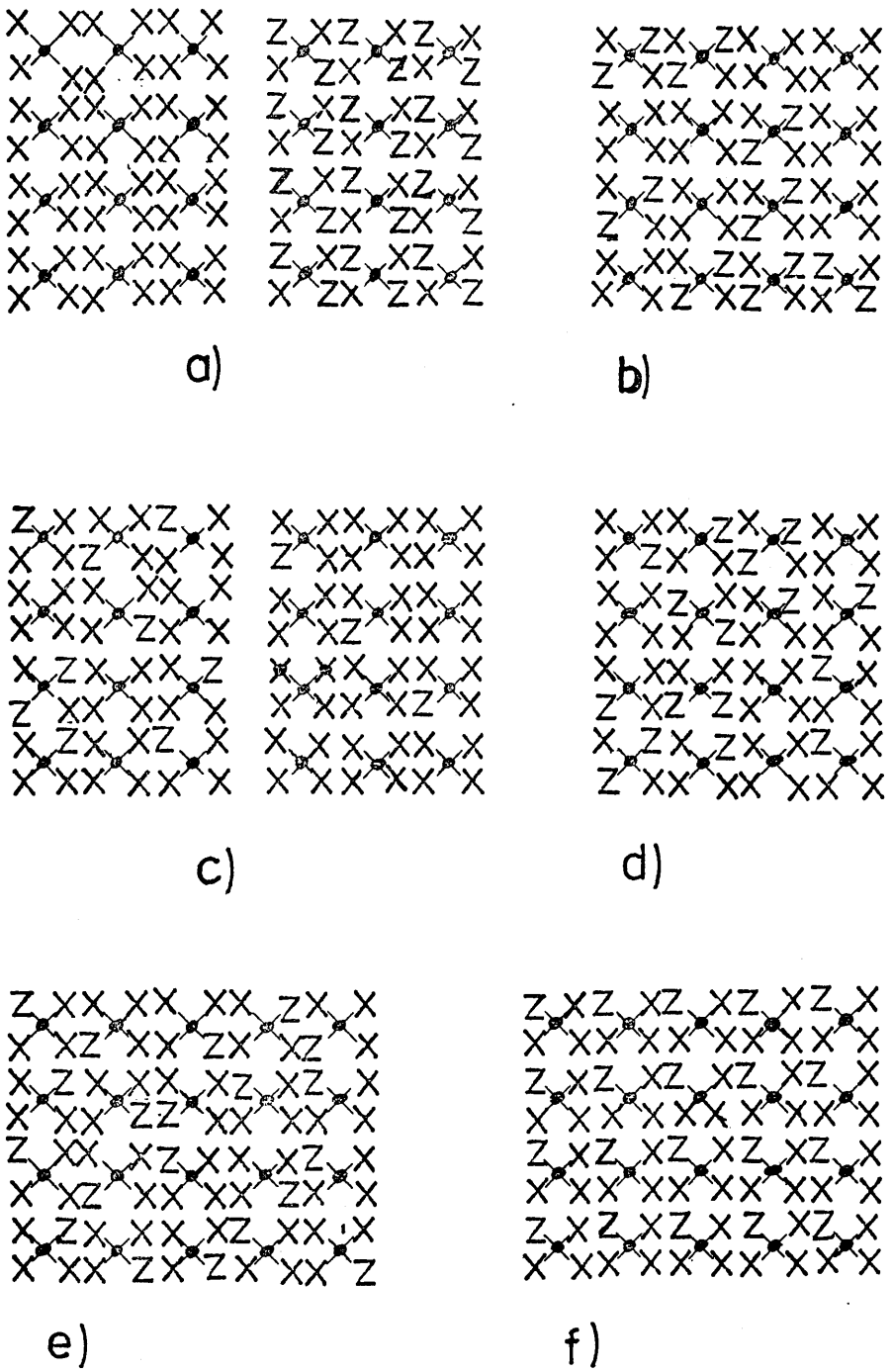


Figure 2:2:1, Possible structures of "MX_3Z" materials

crystalline substances are present with lattice dimensions not those found in the parent compounds MX_2Z_2 and MX_4. I.R. and Raman spectra consist of the superimposed spectra of those of MX_4 and MX_2Z_2 with some broadening of peaks. Only where the vibrational spectra of a material MX_3Z shows strong bands not found in MX_4, or MX_2Z_2, or the x-ray powder photograph lines can all be assigned in terms of a single crystal lattice with fixed dimensions is this possibility excluded.

In "situation d" substitution is totally random. I.R. and Raman spectra are likely to consist of broad lines and powder photographs show only one lattice, but many lines may be missing because of disorder effects.

In "situation e" no dismutation has taken place but the orientation of the molecules is disordered. This situation results in disorder phenomena in the samples' powder photographs, and probably some broadening of lines in the vibrational spectra.

In "situation f" the material consists entirely of ordered MX_3Z molecules. The I.R., and Raman spectra will not be the same as for MX_2Z_2 or MX_4, and Raman bands should be narrow. X-ray powder photographs should show no disorder effects.

Effects of disorder on x-ray powder photographs.[37,38]

A disordered crystal is periodic only in a statistical sense, and frequently a disordered crystal will have a higher symmetry, and give fewer x-ray reflections than the ordered crystal from

which it was derived. In other areas of chemistry, e.g. metals, disordered crystals can be ordered by annealing. As the degree of order in a crystalline material increases the relative intensities of the original, or so-called FUNDAMENTAL reflections will remain unchanged but new reflections, known as SUPERLATTICE reflections will appear. Thus, for example, a monoclinic lattice contains derivative lattices of orthorhombic, and cubic symmetry. A disordered, monoclinic crystal may only show the reflections of a cubic system, but as the order increases extra, superlattice reflections appear, to complete first the orthorhombic, and then the monoclinic reflection patterns.

These disorder phenomena have not been extensively investigated in the chemistry of metal halides. An example is given by the series of compounds $WOCl_4$, $WOCl_3Br$, and $WOBr_4$ (39). Single crystals of $WOCl_4$, and $WOBr_4$ both show all the reflections of the space group I4. In single crystals of $WOCl_3Br$ some superlattice spots are absent, and this, together with the presence in the I.R. spectrum of $WOCl_3Br$ of all bands found in the I.R. spectra of $WOCl_4$ and $WOBr_4$, is taken to indicate a random distribution of bromine atoms in the halogen sites of $WOCl_3Br$. (In fact a totally random distribution does not fit the evidence for this would give the proportion of $WOBr_4$ units as $(1/4)^4 < 1\%$ and the proportion of $WOCl_4$ units as $(3/4)^4 \simeq 30\%$ so that no $WOBr_4$ should be detectable.

In any polycrystalline material other factors, besides those outlined above, may affect the nature of the powder photographs obtained.[37,38] Thermal scattering occurs because of vibrational motions of the atoms in crystals and gives a broad background of scattered radiation which increases in intensity at high scattering angles, and in the region of lattice reflections. Also stacking disorders lead to the absence of lattice reflections at high scattering angles.

The quality of an x-ray diffration powder photograph is also affected by the size of the crystallites. When the size of crystalline particles is below 10^{-6} cm. the observed lines become very broad and it is often not possible to pick out diffraction lines at all. When the particle size is more than 10^{-3} cm. diffraction lines become uneven and spots appear (37).

Thermodynamics of Mixed Halide formation.

Consideration of some simple models does give some understanding of the factors involved in isolation of mixed halides. Of the situations illustrated in figure 2:2:1 a-f only "a" and "f" are fully ordered. If we consider N MX_4Z or N MZ_4X molecules in which the "hetero-bond" (M-Z or M-X respectively) may be orientated in five directions, (this is orientational disorder and is analogous to that shown by MX_3Z molecules in figure 2:2:1e), the number of ways of arranging the units is 5^N.

∴ Entropy of random orientation

$= K \ln 5^N = kN\ln 5 = R\ln 5 = 3.20$ cal deg^{-1} mole^{-1}

$T\Delta S = 0.953$ kcal (kc) mole^{-1} at 25°C (N=Avogadro's number, R= gas constant.

For MX_2Z_3, or MX_3Z_2 molecules the orientational entropy = $k\ln(5X4)^N = kN\ln 20 = R\ln 20 = 5.95$ cal deg^{-1} mole^{-1} and $T\Delta S =$ 1.77 kc mole^{-1} at 25°C.

These quantities are small but may be important where X, and Z are not very different in size, e.g. chloride-fluorides.

In the situation represented by fig 2:2:1d the number of ways of distributing $(1-\theta)n$ X atoms and n Z atoms in n sites is $n!/(n-\theta n)! \times (\theta n)!$ where θ = degree of substitution of x atoms by Z atoms and n=number of halogen atoms present. The entropy of the random structure is given by

$$K\ln W = k\ln \frac{n!}{(n-\theta)!\ (\theta n)!} \qquad (1)$$

Where W= number of possible arrangements. Using Stirlings approximation ($\ln N! = N\ln N - N$) (1) rearranges to

$$k\ln W = -nk[\theta\ln\theta + (1-\theta)\ln(1-\theta)]$$

For a mixed halide MX_xZ_z where all the halogen positions are equivalent the entropy must be calculated per mole of M atoms, but the number of sites is $N_{(x+z)}$ so that the entropy of random substitution is proportional to the total number of halogen atoms. The entropy of random substitution at 25°C may be more than 2 kc mole^{-1} (see figure 2:2:2 b,c,d n=o)

In considering the likely states of mixed halide materials

it is necessary to fix the energies of formation of the individual halides. In fig 2:2:2a three possible cases are considered. If a plot of E^{o}_{f} of the mixed halides against ratio X:Z is a straight line (case 1) there is no thermodynamic energy barrier to dismutation of the mixed halides. If the energy of formation of a mixed halide MX_xZ_{5-x} is greater than that expected by interpolation from the values for MX_5 + MZ_5 (case 2) thermodynamically reorganisation to the latter is favourable. Conversely if a mixed halide MX_xZ_{5-x} has E^{o}_{f} less than that expected by interpolation (case 3) its formation from MX_5, and MZ_5 is favoured.

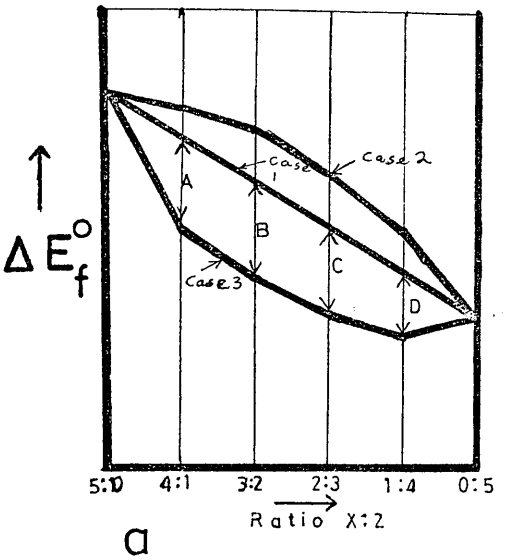
In a randomly substituted mixed halide of a 5valent central atom where the ratio of X;Z atoms is $1-\theta : \theta$ the probabilities of finding the states MX_5— ····· —MZ_5 are as follows

$MX_5=(1-\theta)^5$ $\quad$ $MX_2Z_3=20\theta^3(1-\theta)^2$

$MX_4Z=5\theta(1-\theta)^4$ $\quad$ $MXZ_4=5\theta^4(1-\theta)$

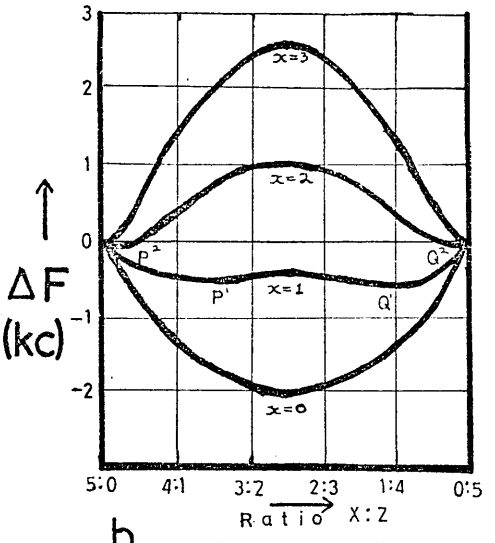
$MX_3Z_2=20\theta^2(1-\theta)^3$ $\quad$ $MZ_5=\theta^5$

Thus by fixing the energy differences (A,B,C,D in fig 2:2:2a) from the interpolated values, (i.e. case 1), for the mixed halides it is possible to calculate free energies of random substitution with respect to non-random, heterogeneous mixtures. The results of these calculations are shown in figures 2:2:2 b,c,d. The curves show the order of stabilisation energies which are required for occurrence of various phenomena.



a

Energies of formation of mixed halides.

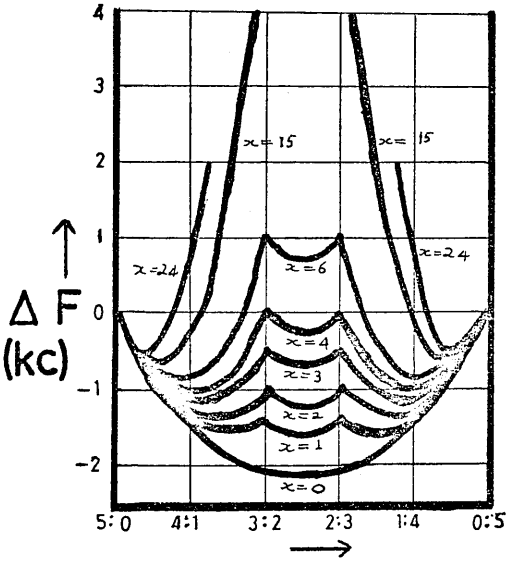


b

A=D=x B=C=2x

Case 2

Free energies of randomners of substitution of mixed halides

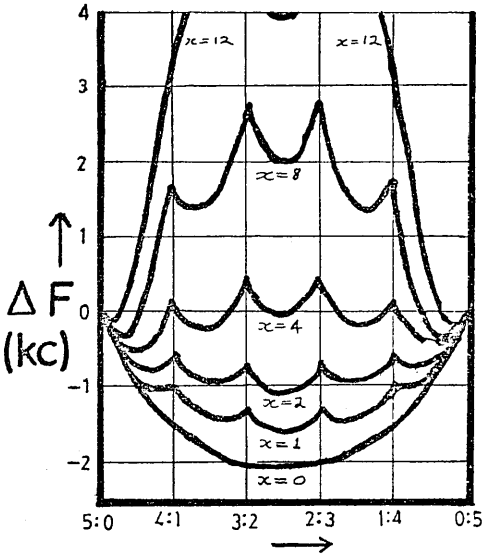


c

A=D=x B=C=2x

Case 3

Free Energies of randomness of substitution of mixed halides



d

A=D=2x B=C=3x

Case 3

Free energies of randomness of substitution of mixed halides

Figure 2:2:2a-d, Thermodynamics of formation of mixed halides.

For instance in figure 2:2:2 b it is seen that the molecules MX_3Z_2, and MX_2Z_3 have to be destabilised with respect to the interpolated E^o_f values by about 6 kc mole^{-1} before complete separation of MX_5, and MZ_5 can be achieved. In case 3 the intermediates MX_2Z_3, and MX_3Z_2 have to be stablised by about 8 kc mole^{-1} before separation of discrete mixed halides can be achieved.

Other, more general points are also indicated by the graphs In case 2 it is seen that situations can exist (when x=1 or 2 and the compositions lie between points P, and Q where separation of mixtures into two phases of composition P, and Q may occur. This is similar to the situation shown in figure 2:2:1c. Another feature of the models chosen for case 3 (fig 2:2:2c,d is that in situations where x, and z in MX_xZ_z are not integers random substitution is often favoured over a heterogeneous mixture whilst the opposite may be true when the ratio is X:Z is such that x, and z are close to integers (see e.g. fig 2:2:2d, x=4)

The above thermodynamic considerations contain some approximations, for instance a random distribution of states has been assumed instead of a Boltzmann distribution, but the basic principles of the discussion are valid and have been used elsewhere (e.g. ref 40). In the discussion of experimental work which follows no conclusions will be derived from this discussion of thermodynamics, but it should be borne

in mind in any discussion of mixed halides.

One more point complicates interpretation of results. A number of systems are known where the phase of a material changes when its composition is changed. e.g. cubic $KTaO_3$ becomes pseudo-monoclinic when 72% of the potassium atoms are replaced by sodium atoms. It is feasible that a random mixture of MX_5, and MZ_5 will give similar behaviour and at intermediate compositions may even exist in phases not found in either of the pure compounds. Thus the fact that a material MX_2Z_3 has a crystal type not found for MX_5, or MZ_5 is not in itself, proof that MX_2Z_3 units are present and that the material is a discrete compound.

Criteria for identification of discrete mixed halides in the solid state.

This author would define a molecular mixed halide compound as a material in which all of the molecules present are of one type. When the proportion of molecules of one type is greater than 95% (say) other molecules may be treated as impurities. At higher levels of other molecules the material must be regarded as a mixture, although at a molecular level. The above discussion suggests that it is virtually impossible to give absolute proof of discrete mixed halides in the solid state. In this work the following criteria will be taken as proof, beyond reasonable doubt of the formation of discrete compounds:-

1) reasonable analytical data,

2) x-ray powder photographs showing the absence of obvious mixtures,

3) vibration spectra showing marked differences between the members of a series MX_xZ_{5-x} (x=1→5).

In addition melting points may be quoted as suggesting the absence of mixtures as is common practice in organic chemistry.

2:3 Nitrogen - Metal - Fluorine Compounds

Analytical data. (see table 2:6:1) and x-ray powder photographs, (see for example fig 2:3:1) both suggest that the materials $MF_3(NEt_2)_2$, $MF_4.NEt_2$ (M=Nb, Ta) and their complexes with Py, and 4Me-Py are discrete compounds. In addition there are marked changes in the I.R. and Raman spectra of the series of materials $MF_{5-x}(NEt_2)_x$ (x=0,1,2 M=Nb,Ta, and their complexes as x is changed and they generally have sharp melting points. The materials may thus, by the definition above, be considered as discrete compounds.

That no more than two fluorine atoms per metal atom may be replaced by NEt_2 groups, under the conditions used may be due to steric factors. Control of the degree of substitution may be either kinetic or thermodynamic. In ammonolysis of the corresponding pentachlorides not all the chlorine may be replaced by nitrogen ligands.[15-18] Similar

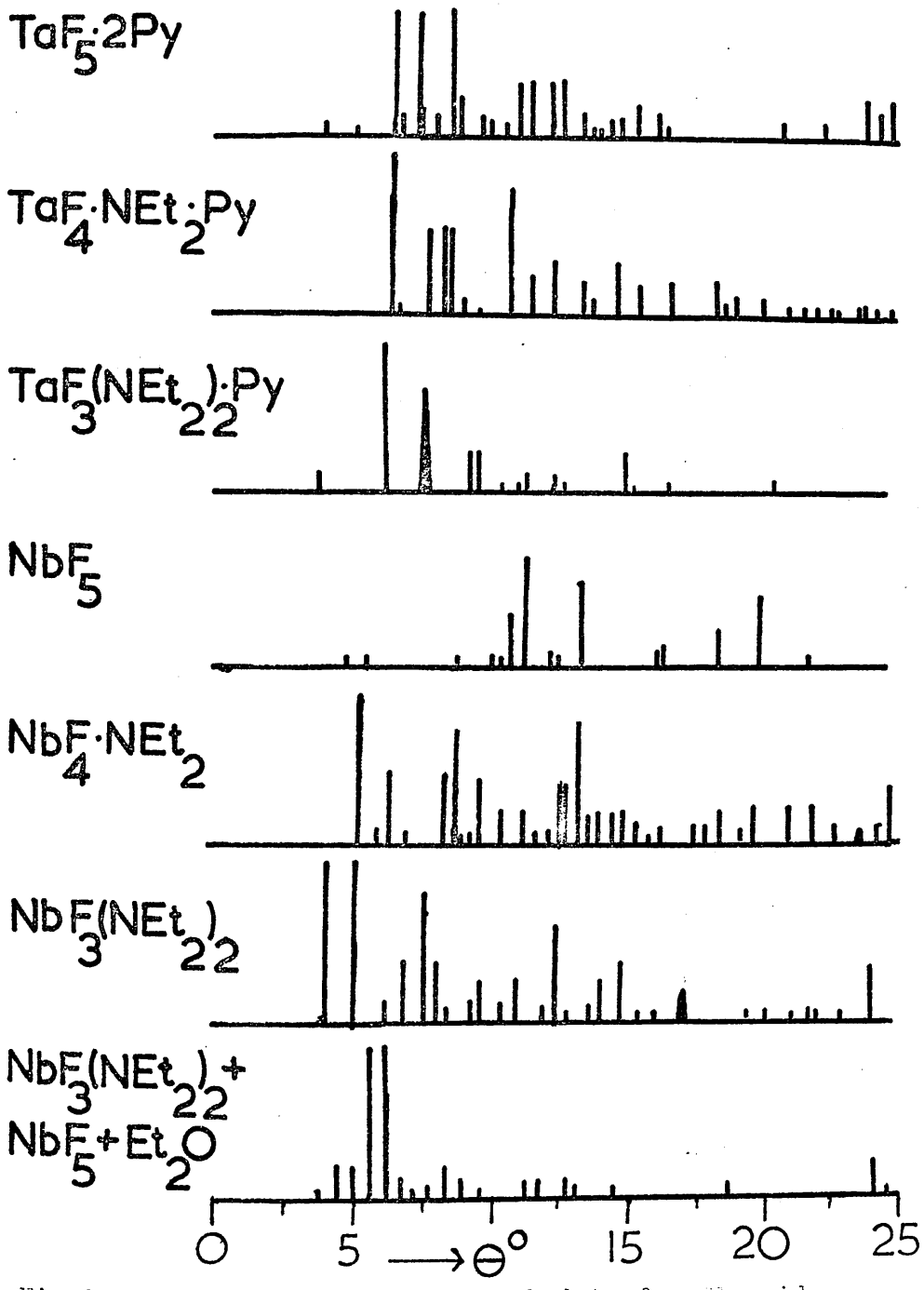
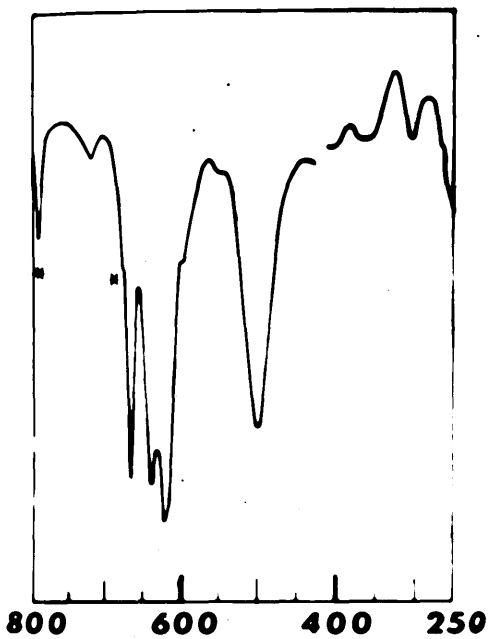


Fig 2:3:1 x-ray powder photograph data for fluoride dialkyl amides (1 indicated broad peaks

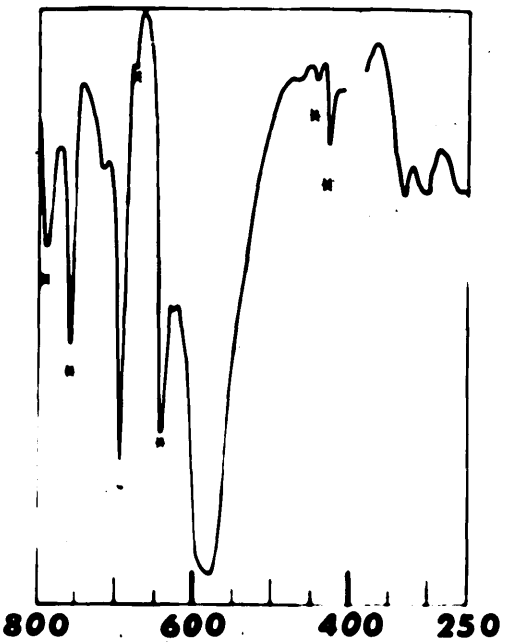
behaviour is found in PF_5 chemistry [49]

The fluoride dialkylamides, and their complexes are coloured (see table 2:6:1). This is not thought to be due to reduction to Nb (IV) or Ta (IV) as these are normally blue, or black if coloured at all.[1] As Nb(V) and Ta(V) have no 'd' valence electrons this colouration is attributed to nitrogen to metal charge transfer. This further suggests that the nitrogen lone pair has symmetry suitable for donation to the metal, and that the nitrogen is planar as in $W(NMe_2)_6$ [36]

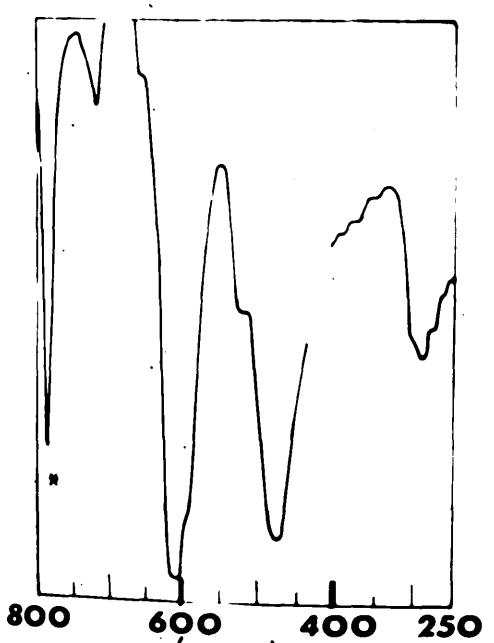
The penta-dialkylamides of niobium, and tantalum are monomeric [35] whilst the pentafluorides are tetrameric.[41] As described in section 1:3 bands in the I.R. spectra of niobium and tantalum fluorides at approximately 500 cm^{-1} may be taken as a diagnostic test for fluorine bridges. Such bands are present in the dialkylamide-fluorides themselves, but absent in their complexes (see e.g. fig 2:3:2). By comparison with $M(NMe_2)_5$ (M=Nb,Ta) and $M(NEt_2)_4$ (M=Ti, Hf)[35] molecules, terminal nitrogen-metal modes are expected at higher frequencies. The shifts of NEt_2 Frequencies between the fluoride-dialkylamides, and their complexes are negligible (see table 2:3:1) and suggest that the NEt_2 groups have similar environment, and configuration in both cases. The strong bands at 458, 480, 475 and 499 cm^{-1} in the I.R. spectra of $NbF_3(NEt_2)_2$, NbF_4NEt_2, $TaF_3(NEt_2)_2$ and TaF_4NEt_2 respectively are thus attributed to metal-



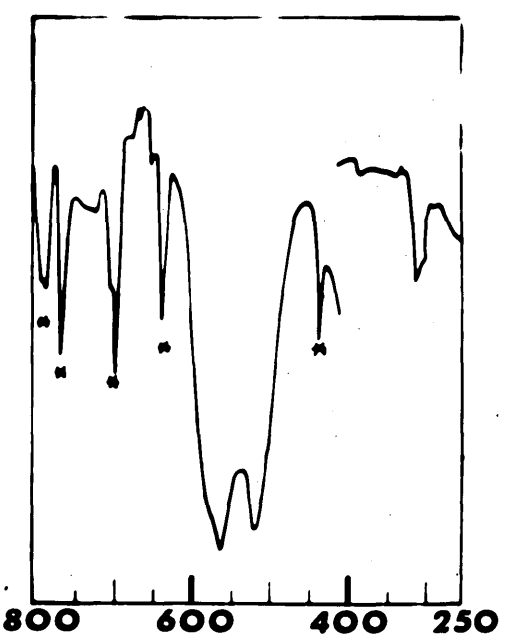
TaF_4NEt_2



$TaF_4NEt_2 \cdot Py$



$TaF_3(NEt_2)_2$



$TaF_3(NEt_2)_2 \cdot Py$

bridging fluorine modes and the fluoride-dialkylamides are presumed to be polymeric. There is no evidence to distinguish between cis, and trans fluoride bridges.

Bradley[35] assigns bands at 998-1003 cm^{-1} and 1150-1160 cm^{-1} in metal dialkylamides to symmetric ($\nu_s NC_2$) and asymmetric ($\nu_{as} NC_2$) C-N-C stretching modes respectively. NR_2 compounds are structurally very similar to OR_2 complexes. The shifts of $\nu_s XC_2$ and $\nu_{as} XC_2$ (X = O,N) between Me_2O and Me_2N compounds are approximately +60 and +35 cm^{-1} respectively (see table 1:6:1 and ref 48) Similar shifts are expected between Et_2O and Et_2N compounds. In Nb(V) and Ta(V) Et_2O complexes $\nu_s OC_2$ and $\nu_{as} OC_2$ are at 820-840 and 980-1000 cm^{-1} respectively so that the assignments of Bradley seem unlikely. In these fluoride-dialkylamide compounds bands at 900-920, and 980-1008 cm^{-1} (see table 2:4:1) are tentatively assigned to $\nu_s NC_2$ and $_{as}NC_2$ on the basis of their intensities and the above arguments.

The formation of a new crystalline phase from mixtures of $NbF_3(NEt_2)_2$ and $NbF_5.OEt_2$ indicates that rearrangement has occurred and a new compound $NbF_{20-x}(NEt_2)_x$ (x=1,2,3,5,6,7) may be isolable but this has not yet been attempted.

That dialkylamide fluorides are weaker Lewis acids than pentafluorides is indicated by the absence of detectable interaction with diethyl ether, or acetonitrile. Steric factors are not thought to be important. In particular the steric

Table 2:3:1 Vibrational spectra of NEt_2 groups in the range 700-1650 cm^{-1} (Frequencies in cm^{-1}

$NbF_4.NEt_2$		$TaF_4.NEt_2$	$TaF_4.NEt_2.Py$, I.R.		$TaF_4.2Py$
NEt_2 bands		NEt_2	NEt_2	Py	I.R.
I.R.	Raman	I.R. bands	bands	bands	bands
	1454(10)			1612s	1609s
1368vw	1380(6)	1364w	1366w	1376vw	
1351w			1358w	1450vs	1450vs
1338vw		1339w		1243w	1238w
1324w		1330w	≠	1220w	1220w
1272mw		1276w	1278w	1159w	1156vw
1189m	1187(15)	1193ms	1193m	1069s*	1070s
1124s		1126	1130m	1044s*	1045m
1092ms		1093ms	1095mw		1017)s
					)
1069ms	1071(7)	1071m	1069s*	1008s,b	1015)
1035ms	1033(7)	1043ms	1048s*	956w	950w
994s	994(30)	1004(s)	1008s,b*		870w
907sh		905w		762s	760s
901s,asy	898(40)	917ms	906s,asy	697s	690s
793ms	790(8)	794ms	792m		

* indicates band used more than once

≠ The only additional band in this region was a very weak band at 1230 cm^{-1}

requirements of acetonitrile as a ligand are very small. The weaker Lewis acidity may be due to nitrogen-metal $p_\pi \rightarrow d_\pi$ bonding as has been suggested by Bradley[35] although the relative strength of metal-fluorine bridging bonds in fluorides, and dialkylamide-fluorides may be important.

No compounds were isolated from reactions of MoF_5 and Me_3SiNEt_2 and some disproportionation to Mo(VI) and Mo(IV) may have occurred.

Analytical data suggests that although some substitution for fluorine by NMe groups was achieved in the reaction between $(Me_3Si)_2NMe$ and pentafluorides no pure compounds have yet been obtained. This may have been due to the presence of $NHMe_2$, or $Me_3SiNHMe$ in the $(Me_3Si)_2NMe$, which is difficult to purify.

2:4 Fluoride-Chlorides, and Fluoride-Bromides

Reactions between Me_3SiCl, or Me_3SiBr, and NbF_5 are far more complicated than reactions of dialkylamides because:-

a) The mixed fluoride bromides, or fluoride-chlorides show more tendency to reorganise than fluoride dialkylamides.

b) Using Me_3Si-halides substitution for all five fluorines by chlorine, or bromine is possible, whilst only two fluorine atoms may be substituted by NEt_2 groups.

c) The acceptor power of the pentahalide is not greatly decreased by introduction of chloride, or bromide, and a precipitating ligand must be added to solutions in diethyl ether to isolate the mixed halide.

The presence of extra lines in the ^{19}F.N.M.R. spectra in the supernatant liquor in a mixture of composition $NbCl_{2.2}F_{2.8}.OEt_2$ indicated that more than one fluorine-containing niobium species is present. The ^1H spectrum shows only one triplet-quartet pattern for OEt_2 groups. This suggests that the exchange mechanism for ether molecules is intermolecular whilst that for F atoms must be intramolecular, for otherwise only one ^{19}F resonance would be observed (as in NbF_5-TaF_5 mixtures, see section 1:5).

In solution in ether the chloride-fluorides of niobium seem to be subject to easy reorganisation and a degree of randomness of substitution. On precipitation only $NbCl_5.OEt_2$

is isolated but this does not necessarily mean that it is the predominant species in solution .

When pyridine is added to the chloride-fluoride-ether solutions the system becomes more complicated. It is not known whether the precipitates reflect the equilibrium in the 1:1 complexes or the 1:2 pyridine complexes. Analysis of the materials $NbCl_{0.5}F_{4.5}.2Py$, $NbClF_4.2Py$, $NbCl_2F_3.2Py$, $NbCl_3F_2.2Py$, and $NbCl_5Py$ are all consistent with the presence of single compounds. Interpretation of x-ray powder photograph data is more difficult. No lines were detected with scattering angle greater than 20° and a degree of thermal scattering was found. Such behaviour may be due to stacking faults, crystal disorder, thermal motions, imperfect sampling, or a combination of all four. The powder photograph lines cannot be indexed, but the intensity patterns of the lines suggest that $NbCl_{0.5}F_{4.5}.2Py$, $NbClF_4.2Py$, and $NbCl_2F_3.2Py$ are probably isostructural (see fig 2:4:1). In no cases do mixtures appear to be present. The material designated $NbCl_4F.2Py$ is not isostructural with any of the other materials obtained.

The changes in I.R. and Raman spectra in the series of materials $MCl_xF_{5-x}.2Py$ (x=0, 0.5,1,2,3,4,5.) are not sufficient to state that a series of chloride-fluorides have been isolated. Taking all the evidence together it seems certain that the degree of randomness of substitution in these 1:2 materials is not as great as in solutions of the 1:1 complexes; but it

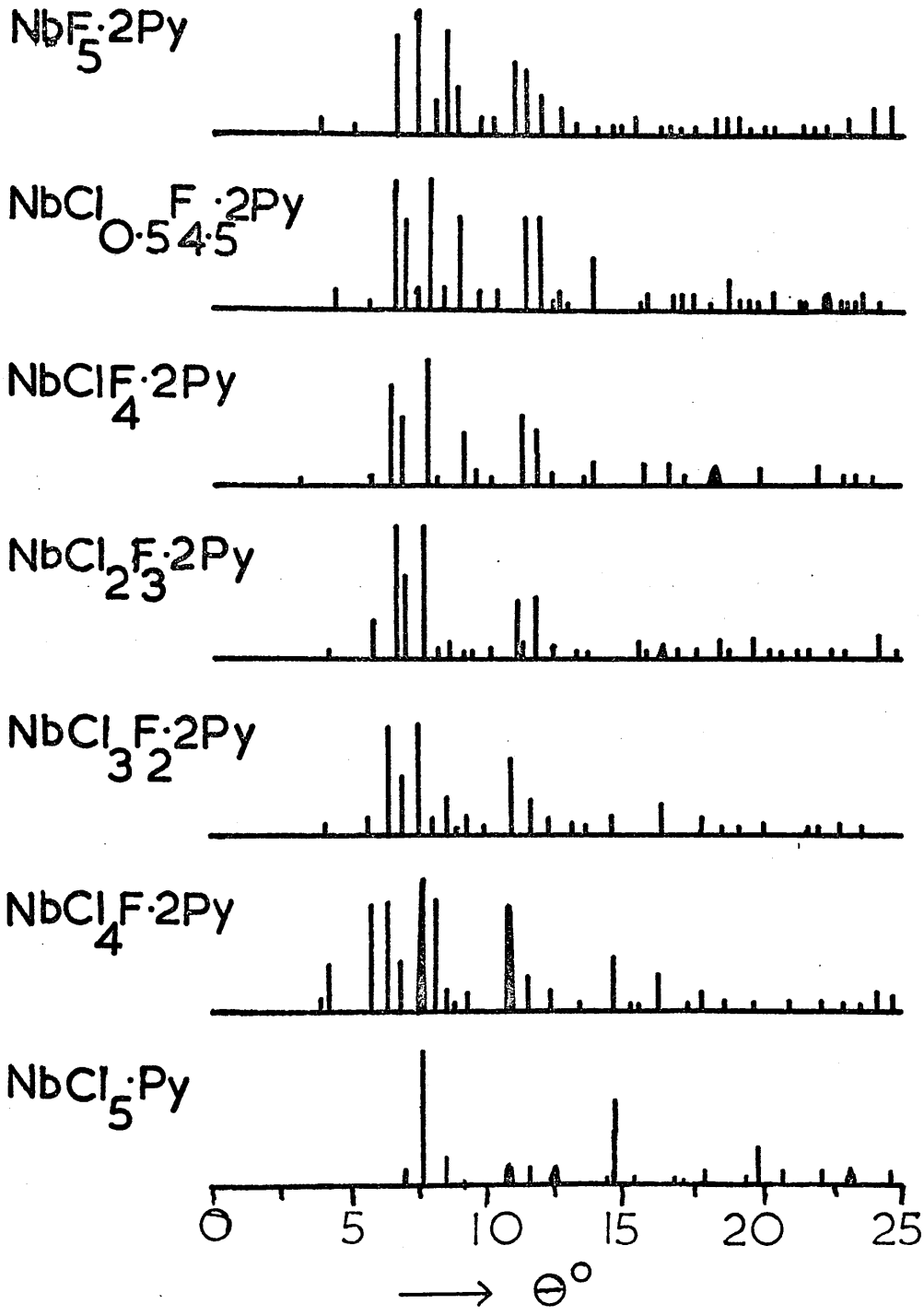


Figure 2:4:1 X-ray powder photographs of Chloride-Fluoride Pyridine complexes.

is not possible to say which of the materials obtained, if any, are discrete compounds.

Niobium pentachloride can be reduced by pyridine (see sections 1:1, 2:6). In the chloride-fluoride-pyridine systems changes in colour from yellow to green, and then to brown or black, are taken to be indicative of reduction of Nb(V), to Nb(IV) as Nb(IV) compounds are often brown or black.[1] Reduction of $NbCl_5$ detected in this way was observed only in the presence of free pyridine, in solution, or at high temperatures. No reduction was observed visually when the ratio of Cl:F was less than 3:2 but it may have been a factor in the imperfect analysis of the material $NbCl_4F.2Py$. $NbCl_5.Py$ could only be made in small quantities when excess pyridine could be rapidly removed under vacuum.

Because $NbBr_5$ is more reactive than $NbCl_5$ attempted preparations of fluoride bromides were carried out using CH_3CN rather than Et_2O as a solvent. The isolation of almost pure $NbBr_5.CH_3CN$ from a solution with 1:1 ratio of NbF_5:Me_3SiBr suggests that either reorganisation reactions occur readily, or that bromination becomes faster as more bromine atoms replace fluorine atoms. The large number of washings needed to isolate $NbBr_5.CH_3CN$, and the presence of only small quantities of the yellow material at any one time suggest that the degree of substitution is nearly random and $NbBr_5.CH_3CN$ is only isolable because of its lower solubility in CH_3CN, and rapid reorganisation reactions.

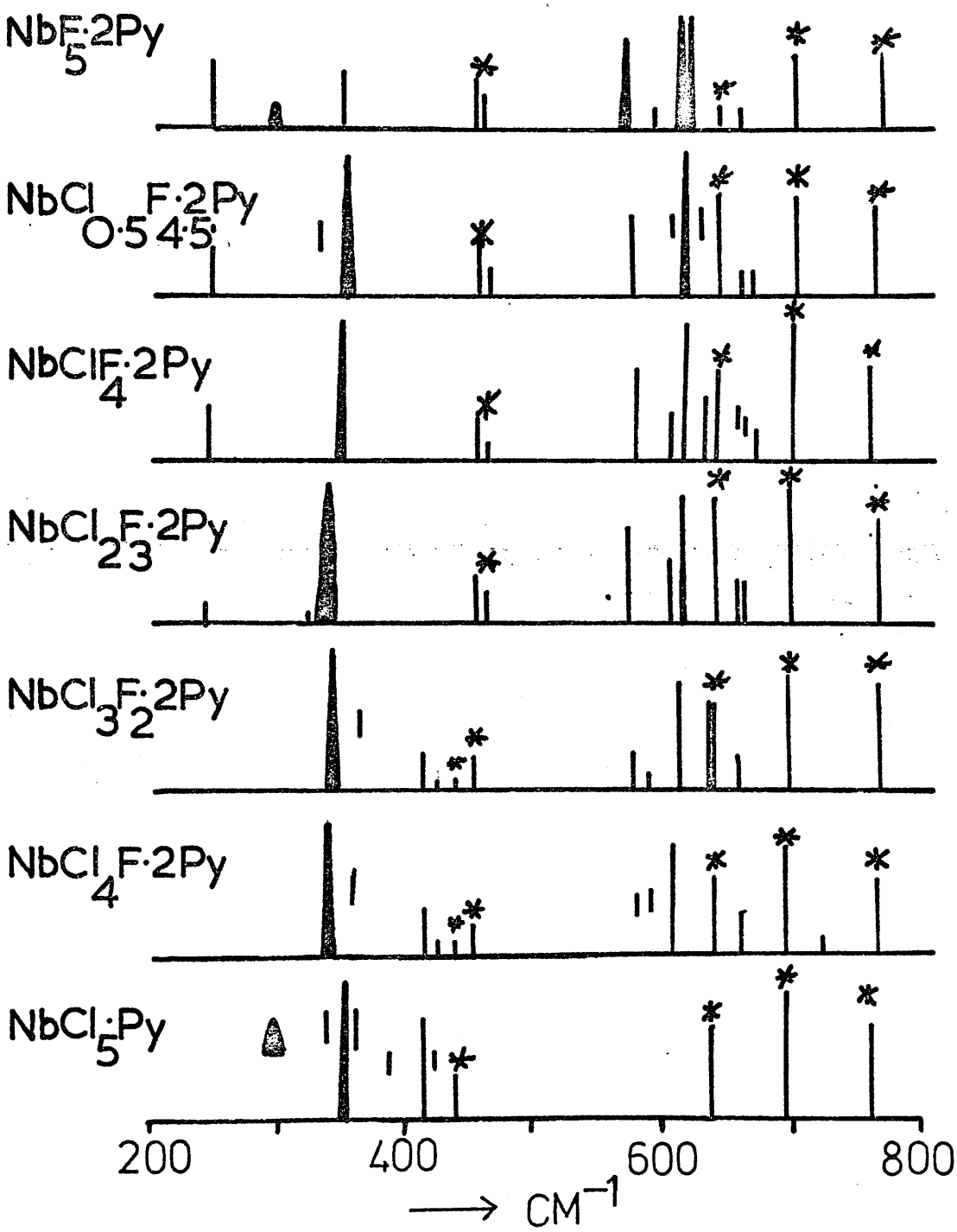


Figure 2:4:2 I.R. spectra of Chloride-fluoride-pyridine complexes.

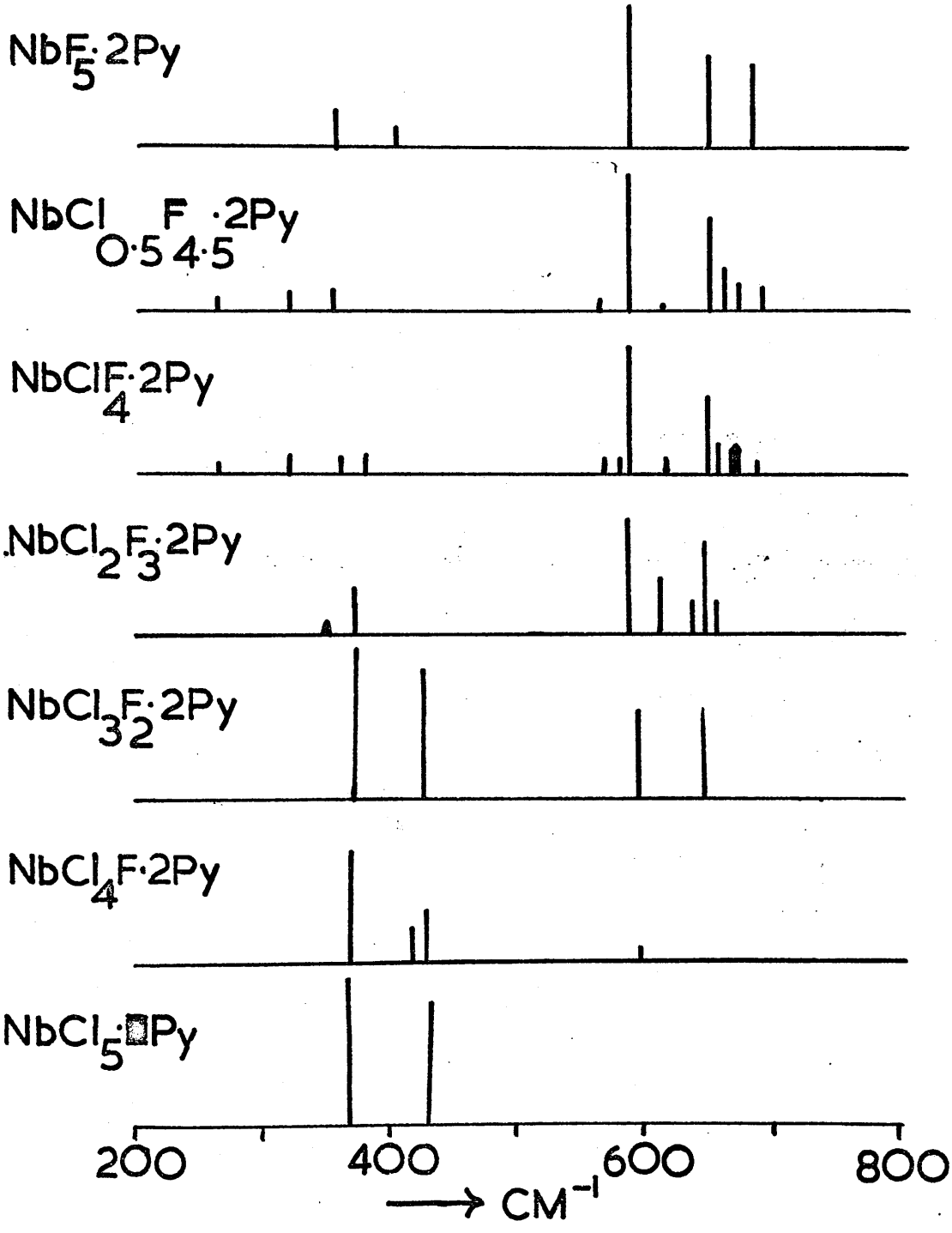


Figure 2:4:3 Raman spectra of Chloride-Fluoride-Pyridine complexes.

2:5 Other Substitution Reactions

Production of Me_3SiF by reactions of pentafluorides with Me_3SiCN, Me_3SiNCO, or Me_3SiNCS suggests that some substitution reactions have taken place in each case. In all cases the I.R. spectra indicate that pseudohalide units have remained intact and are bonded to the metal but analyses are imperfect and indicate the absence of pure compounds. All the fluorine attatched to the metal can be replaced in reactions with Me_3SiNCS, or Me_3SiNCO. [illegible] In the reaction of $NbF_5.OEt_2$ and Me_3SiNCS no intermediate fluoride-thiocyanates could be isolated and analysis suggested that almost pure $Nb(CNS)_5$ was obtained from an ether solution containing a 1:1 ratio of Me_3SiNCS: $NbF_5.OEt_2$. This reorganisation did not occur in the reaction of TaF_5 with Me_3SiNCS. In the cyanide reactions not all the fluorine could be replaced. The strong band at 2200 cm^{-1} in the I.R. spectra of the material is consistent with the presence of either bridging, or terminal carbon-bonded C≡N groups.[42,45]

The failure to isolate pure fluoride cyanates, thiocyanates, and cyanides of niobium and tantalum is surprising in view of the existence of chloride cyanates, thiocyanates, and cyanides of niobium.[4-9] It is possible that other preparative methods (see section 2:1) or changes of experimental conditions might lead to successful isolation of the fluoride-compounds.

The only other substitution reaction attempted was that of $(Me_3Si)_2O$ and NbF_5 which gave a product with analytical data, and I.R. spectrum consistent with $NbOF_3$. $NbOF_3$ can be made by the reaction $4NbO_2F \longrightarrow Nb_3O_7F + NbOF_3$ at 700°C.(46) $TaOF_3$ has been reported as a product of the reaction of TaF_5 and silica at 400°C, but no further information has been reported.(47) These high temperature methods of preparation yielded crystalline products, but the absence of crystalline material in the products of reaction of NbF_5 with $(Me_3Si)_2O$ does not exclude the possible presence of $NbOF_3$. Interpretation of the I.R. results is difficult because the bands are very broad (see fig 2:5:1)

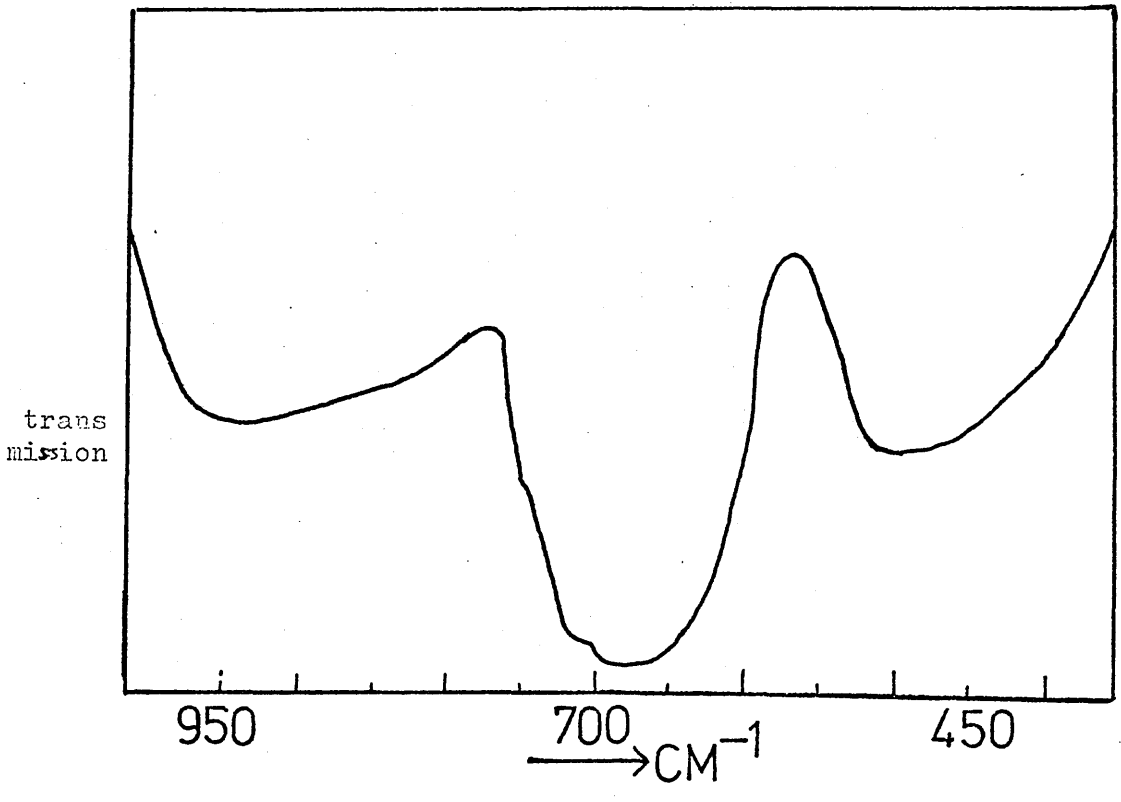


Fig. 2:5:1 I.R. spectrum of "$NbOF_3$"

These broad bands, and the absence of lines in the x-ray powder photographs are consistent with the presence of a mixture. However large I.R. bandwidths are consistent with strong oscillator effects (discussed in section 1:6) which would be expected in $NbOF_3$ which must have bridging oxygen or fluorine atoms and strongly interacting bond dipoles. The blue colouration formed in exposure of the material to light may be due to reduction of the niobium by some organic residues present, or to production of vacancy sites in the $NbOF_3$ lattice. No further work was done to characterise these products, but it might be possible to achieve this by formation of Lewis acid-base complexes.

2:6 Experimental

Preparation of reagents:—

NbF_5, TaF_5, MoF_5:- See Appendix 1

Me_3SiCl:- Fluka, puriss grade, kept over freshly activated 3 Å Molecular sieve $NHEt_2$:- B.D.H., shaken three days over fresh, crushed sodium hydroxide.

Me_3SiNEt_2:- made in vacuo by the reaction $Me_3SiCl+2NHEt_2 \rightarrow Me_3SiNEt_2+NH_2Et_2Cl$. The reactions is reversible and some of the NH_2Et_2Cl precipitated as a white solid is always carried over in distillations of Me_3SiNEt_2. The Me_3SiNEt_2 was vacuum distilled (seventeen times) until no white solid appeared and no $NHEt_2$ or $NHEt_2^+$ could be detected in the ^1H N.M.R. spectrum of the Me_3SiNEt_2.

Me_3SiH:- Alfa Inorganics.

Me_3SiBr:- Me_3SiH and bromine (Analar) were condensed together in stoichiometric quantities and allowed to warm to room temperature at which temperature the reaction $Me_3SiH+Br_2 \rightarrow Me_3SiBr+HBr$ occurred. The product was distilled and trapped at -63°C in a dynamic vacuum so that HBr was removed, twice vacuum distilled onto freshly activated 5 Å molecular sieves to remove any residual Me_3SiH and HBr, and kept over 5 Å molecular sieves. The ^1H N.M.R. spectrum showed only one resonance at 9.47τ. AgCN:B.D.H.

Me_3SiCN:- Me_3SiBr was refluxed with AgCN and the Me_3SiCN was

fractionally distilled

$$Me_3SiBr + AgCN \rightarrow Me_3SiCN + AgBr$$

(B.P. 115-117°C. The ^1H N.M.R. spectrum showed only one peak at 10.09 τ)

$(Me_3Si)_2O$:- Me_3SiCl was reacted with H_2O

$2Me_3SiCl + H_2O \rightarrow (Me_3Si)_2O + 2HCl$ and the $(Me_3Si)_2O$ fractionally distilled (B.P. 109-10°C) The product was dried over NaOH and portions of fresh sodium until the sodium did not tarnish. The ^1H N.M.R. spectrum showed one peak at 9.94 τ.

AgCNO:- made by the reaction

$AgNO_3 + KCNO \rightarrow AgCNO + KNO_3$ was washed with water, then ethanol and dried 150°C.

AgCNS:- prep as for AgCNO using KCNS instead of KCNO.

Me_3SiCNO:- Me_3SiCl was refluxed with AgCNO

$$Me_3SiCl + AgCNO \rightarrow Me_3SiCNO + AgCl$$

and the products fractionally distilled, B.P. 90-91°. The product was dried over freshly activated molecular sieve.

Me_3SiCNS:- Me_3SiCl was refluxed with AgCNS and the product fractionally distilled, (B.P. 140-142°C)

$$Me_3SiCl + AgCNS \rightarrow Me_3SiCNS + AgCl.$$

The product was dried over two successive portions of freshly activated 4 Å molecular sieves, and stored over a third portion. The ^1H N.M.R. spectrum showed only one peak at 10.06 τ

NH_2Me:- B.D.H., shaken two days at 20°C over fresh crushed NaOH.

$(Me_3Si)_2NMe$:- made by the reaction,

$$2Me_3SiCl+3NH_2Me \rightarrow (Me_3Si)_2NMe+2NH_3MeCl,$$

by passing NH_2Me through Me_3SiCl at -78^oC. The product was distilled off, and fractionally distilled (B.P. 148-149°C) The material may have been contaminated with a little free $NHMe_2$, and Me_3SiCl as the reaction is to some extent reversible. Et_2O, CH_3CN, Py, 4Me-Py, and Me_2SO were purified as in section 1:9.

Preparation of fluoride-dialkylamide compounds, and their complexes with pyridine and 4Me-Pyridine.

Me_3SiNEt_2 was vacuum distilled onto the pentafluoride in a pyrex flask, and the reaction mixture warmed to room temperature and shaken under vacuum for three days. After eight hours the reaction had produced viscous liquids, immiscible with excess Me_3SiNEt_2, which reacted further with Me_3SiNEt_2 to give solids. The Me_3SiF formed (identified by I.R.) and unreacted Me_2SiNEt_2 were pumped off and the solids were crushed in the inert atmosphere box. More Me_3SiNEt_2 was vacuum distilled onto the solids, and the mixture again shaken for three days. When the volatile fraction was pumped away analytical data showed the solids to be $MF_3(NEt_2)_2$ (Table 2:6:1).

MoF_5 took considerably longer to react and was shaken for two periods of one week. A black solid was formed which gave the analysis C = 14.4, H = 2.9, N = 4.1, F=31.8%

$MoF_4.NEt_2$ requires C = 19.7, H = 4.1, N = 5.7, F = 31.1%

Table 2:6:1

Analytical Data for metal-fluoride-nitrogen compounds

compound		ANALYSIS H	C	N	M	F	Melting, decomposition Temps, colours
$TaF_4.NEt_2$	found	54.8	14.7	3.7	4.2	22.5	m-123°C, pale yellow
	calc	55.0	14.6	3.1	4.3	23.1	volatile 175°C, d-260°
$TaF_3.(NEt_2)_2$	found	48.1	24.4	5.2	7.6	14.9	m-203°C, yellow
	calc	47.3	25.1	5.3	7.3	14.9	
$NbF_4.NEt_2$	found	37.8	19.8	4.3	5.9	31.2	m-150°C, orange,
	calc.	38.6	19.3	4.2	5.8	31.5	d-170°C
$NbF_3.(NEt_2)_2$	found	31.1	32.2	6.8	9.4	19.8	m-82°C, scarlet
	calc	31.6	33.7	6.9	9.5	19.4	d-120
$TaF_4.NEt_2.Py$	found	44.9	26.0	3.6	6.7	19.1	m-115°C, yellow
	calc	44.3	26.5	3.7	6.9	18.6	d-300°C
$TaF_3.(NEt_2)_2.Py$	found	39.9	32.9	5.3	9.2	13.7	m-51°C, brown,
	calc	39.2	33.8	5.5	9.1	12.4	crystalline
$NbF_3.(NEt_2)_2.PY$	found	24.5	41.7	6.8	11.3	14.8	m-56°C
	calc	24.9	41.8	6.9	11.3	13.3	
$TaF_4.NEt_2.4MePy$	found		28.7	3.4	6.7	18.4	m-122°C, yellow,
	calc		28.5	4.0	6.6	18.0	d-210°C
$TaF_3.(NEt_2)_2.4MePy$	found	37.9	35.9	5.5	9.0	11.9	light brown
	calc	38.1	35.4	5.7	8.8	12.0	liquid
"$TaF_3.NMe$"	found		9.8	2.7	4.7	18.9	yellow
$TaF_3.NMe$	calc		4.5	1.1	5.2	21.4	
$TaF_3.(NMe)_2$	calc		9.3	2.3	10.9	7.4	
"$NbF_3.NMe$"	found		6.3	1.8	4.4	35.7	yellow
	calc		6.7	1.7	7.8	32.0	
"$Ta_2F_8.NMe$"+Et_2O	found		13.7	3.1	2.1	19.7	pale yellow
$Ta_2F_8.NMe$	calc		2.3	0.6	2.7	24.7	
$Ta_2F_8.NMe.(OEt_2)$	calc		1.59	1.9	2.1	22.3	
"$TaF_3.NMe$"+Py	found		26.0	3.2	7.6	16.9	yellow
$TaF_3.NMe.Py$	calc		22.1	2.9	7.4	20.0	

Reaction between niobium, or tantalum pentafluoride, dissolved in diethyl ether, and Me_3SiNEt_2 produced orange, or yellow solutions respectively, which, when shaken after two hours produced orange, or yellow precipitates respectively. Quantities of reactants used in typical reactions (in m. moles) were

$NbF_5 : Et_2O : Me_3SiNEt_2 = 11.73 : 24.23 : 11.26$

$TaF_5 : Et_2O : Me_3SiNEt_2 = 18.4 : 62.3 : 13.2$

The solids that precipitated from this reaction were washed with the liquid mixture of Et_2O and Me_3SiF present to remove excess pentafluoride.

Acid-base complexes of the fluoride-dialkylamides were prepared by vacuum distilling pyridine, or 4 Me-pyridine onto the dialkylamide, allowing it to react, and pumping off excess base. No interaction was observed between the niobium, or tantalum fluoride-dialkylamides and acetonitrile, or diethyl ether.

Reaction between NbF_5 and Me_3SiCl.

When Me_3SiCl (6.8 m moles) was added to NbF_5 (3.2 m moles) a yellow solid and Me_3SiF (identified by I.R. spectroscopy) were formed. When the solid was heated to approximately 140°C in vacuo a viscous yellow liquid distilled off which did not solidify for three days. The products of this reaction were not further investigated.

Other NbF_5-Me_3SiCl reactions were carried out in solution in diethyl ether. The Me_3SiCl was normally added in stoichiometric

TABLE 2:6:2

Quantities of reactants used in reactions between NbF_5 and Me_3SiCl (all quantities in m moles)

Compound desired	NbF_5	Et_2O	Me_3SiCl	Py	exp N°
$Nb_2ClF_9.4Py$	13.85	21.6	6.91	xs	1
$NbClF_4.2Py$	6.68	33	6.68	xs	2
$NbClF_4.2Py$	4.20	32.2	4.20	35	3
$NbCl_2F_3.2Py$	7.24	22.3	14.46	19	4
$NbCl_3F_2.2Py$	7.97	25	23.81	18	5
$NbCl_4F.2Py$	6.09	32.9	24.3	xs	6
$NbCl_5.Py$	7.72	22	41.5	xs*	7
$NbCl_4F.Et_2O$	8.24	8.35	32.35	-	8
$NbCl_5.Et_2O$	7.76	33.3	41.9		9
$NbCl_4F.Et_2O$ from "$NbCl_3F_2.Et_2O$"	9.34	8.1	25.2		10
$NbCl_5.Py$ from "$NbCl_4F.Et_2O$" *	9.37	13.99	31.96	6.3	11
	9.37	13.99	31.96		

xs indicates that more pyridine was added than was enough to precipitate all the niobium species.

* in this experiment pyridine was added to a small portion of the $NbCl_5.Et_2O$ and the mixture was pumped dry before it was washed with ether.

Table 2:6:3

Analysis of niobium chloride-fluoride complexes

exp	compound	%	C	H	N	Cl	F	Nb
1	$NbClF_9.4Py$	found	32.9	3.4	7.7	4.8	24.4	
		calc	33.9	2.9	7.9	5.0	24.1	
2	$NbClF_4.2Py$	found	33.0	3.0	7.8	10.0	20.7	
		calc	33.1	2.8	7.7	9.8	21.0	
4	$NbCl_2F_3.2Py$	found	31.7	3.0	7.4	18.4	14.9	24.5
		calc	31.7	2.7	7.4	18.7	15.0	24.5
5	$NbCl_3F_2.2Py$	found	28.7	2.8	6.7	28.9	9.3	23.3
		calc	30.4	2.5	7.1	28.9	9.6	23.5
	$NbCl_3F_2.Py$	calc	19.0	1.6	4.4	33.6	12.0	29.4
6	$NbCl_4F.2Py$	found	27.7	2.5	6.9	32.6	5.9	
		calc	29.1	2.5	6.8	34.4	4.2	
	$NbCl_4F.Py$	calc	18.0	1.5	4.2	42.6	5.7	
	$NbCl_4.2Py$	calc	30.6	2.6	7.1	36.1	0.0	
7	$NbCl_5.Py$	found	17.6	1.7	3.9	50.0	0.2	26.7
		calc	17.2	1.4	4.0	50.8	0.0	26.6
9	$NbCl_5.OEt_2$	found	13.9	3.1		51.7	0.3	26.5
		calc	13.9	2.9		51.5	0.0	27.0
10	$NbCl_4F.OEt_2$	found	15.3	2.9		41.7	3.6	
		calc	14.7	3.1		43.3	5.8	
8	"$NbCl_4F.OEt_2$"	found	13.7	3.1		45.8	2.0	
11	"$NbCl_5.Py$"	found	17.5	1.7	4.1	45.8	2.4	

quantities in an attempt to prepare mixed chloride-fluorides. A yellow precipitate was formed in these reactions when both the ratio of $Nb:Et_2O$ <0.9 and of $Me_3SiCl:Nb$>3. In attempts to precipitate solids which could be washed by the ether and Me_3SiF present, pyridine was added to the reaction mixtures. The quantities (in millimoles) used in a series of reactions are given in table 2:6:2. All the chloride-fluorides prepared were yellow, and the intensity of colouration increased as the number of chlorine atoms increased. Melting (m) and decomposition (d) temperatures (°C) were

$Nb_2ClF_9.4Py$ m166°, $NbClF_4.2Py$ m148°, $NbCl_2F_3$ d 126°, m140°, "$NbCl_3F_2.2Py$" m56° "$NbCl_4F.2Py$" d123°, $NbCl_5.Py$ m,d,220°, $NbCl_5.Et_2O$ m80°, d110°, "$NbFCl_4.Et_2O$" (experiment 10) m66°.

Reactions between NbF_5 and Me_3SiBr.

To 5.72 m moles NbF_5 was added 92.7 m moles CH_3CN and 5.73 m moles Me_3SiBr. A mixture of a purple solid and what appeared to be only a little yellow solid which was moderately soluble in CH_3CN precipitated. The CH_3CN was decanted into one compartment of the two compartment vessel in which the reaction was carried out (see appendix 1) and the CH_3CN was pumped away to yield a yellow solid. This solid gave the analysis C=9.7, H=1.4, N=4.4, Br=7.4, F=34.5%

$NbF_5.CH_3CN$ requires C=10.5, H=1.3, N=6.1, F=41.5%

$NbF_4Br.CH_3CN$ requires C=8.3, H=1.0, N=4.8

Br=27.6 F=26.2% The yellow product gave the following I.R. absorptions (all frequencies in cm^{-1}) 2324s, 2298s, 1368mw, 1032mw, 951m, 704s, 665vs,vb, 415mw.

Many washings were required to decrease the proportions of yellow: purple solids (estimated visually) in the residues. After about a dozen washings the purple solid could still be seen to contain traces of yellow solid. It gave the analysis C=4.4, H=0.7, N=2.5, Br=71.8, F 0.3: $NbBr_5.CH_3CN$ requires C=4.5, H=0.6, N=2.6, Br=74.9, F=0% The purple solid gave I.R. absorptions as follows (frequencies in cm^{-1}) 2312s, 2284s, 1358ms, 1020m, 947m, 799w, 660mw, 604w, 250s,b

Reactions between NbF_5 and Me_3SiCN.

a) To 4.38 m moles NbF_5 were added 20.25 m moles Me_3SiCN, a white-grey solid, and Me_3SiF (identified by I.R. spectroscopy) were formed. The solid gave the analysis C=12.0, H=1.0, N=9.4, F=25.7% suggesting a C:N mole ratio of 1:0.7. NbF_4CN requires C=6.2 H=0 N=7.2 F=39.0%. $NbF_3(CN)_2$ requires C=11.9 H=0 N=13.9 F=28.2% The solid gave the following I.R. absorptions (all frequencies in cm^{-1}) 2200s, 1265m, 1020w, 890w, 870mw, 852m,b 710m,vb, 660s,vb,500m,b, X-ray powder photography showed the solid to be amorphous.

b) To 5.26 m moles NbF_5 were added 30m moles CH_3CN and 5.28 m, moles Me_3SiCN. A finely powdered grey-brown solid was formed which was too fine to be washed by decantation and charred at 198°C when heated in vacuum, to give a black oil. The solid gave the

analysis C=11.7, H=1.3, N=10.2, F=30.4%. $NbF_4CN.CH_3CN$ requires C=15.3, H=1.3, N=11.9, F=32.2%. The I.R, spectrum showed the following absorptions (all frequencies in cm^{-1}) 2320vs, 2298vs, 2198s,b, 1368w, 1030mw, 950w, 7065, 660vs,vb, 500b,m 240, s.

Reaction of Pentafluorides with Me_3SiNCS.

a) To 3.27 m.moles NbF_5 were added 10.2 m.moles Et_2O and 3.30 m.moles Me_3SiNCS. The mixture reacted to give a black solution after eight hours which precipitated a black, crystalline material which was a red-brown colour when ground. The solid gave the analysis C=22.9, H=2.4, N=15.3, S=33.0, F=0% $Nb(NCS)_5$ requires C=15.7, H=0, N=18.3, S=41.8, F=0%. $Nb(NCS)_5.Et_2O$ requires C=23.6, H=2.2, N=13.6, S=35.1, F=0%. The material did not give a good I.R. spectrum but showed the following absorptions. (all frequencies in cm^{-1}) 2020mw, 1950vs,b, 1900vs,b, 1860vs,b, 1184w, 1080w, 1000w, 982w,943mw, 924m, 876mw, 825mw, 755m, 560mw, 335b,vs. A solution of the material in Nujol showed the I.R. absorptions 2064s, 1960mw, 1259mw, 920-970b,w, 859m, asy, 760w, 720m, 630m. Me_3SiNCS gives the following I.R. absorptions:- 2964s, 2900w, 2520m,b 2180w, 2060b,vs, 1955m, 1410m,b, 1335w, 1260s, 1050mw, 985sh, 950s, 899s, 820s, 750s, 700m, 630s, 435vs,b.

b) To 11.83 m.moles NbF_5 were added 8 m.moles Et_2O and 11.2 m.moles Me_3SiCNS. The solution reacted over several hours

to give a black solid which was a red-brown colour when ground and gave the following analysis .Nb=20.7, C=22.3, H=2.5, N=12.8, S=30.0, F 0.2%. $Nb(NCS)_3.OEt_2$ requires Nb= 20.3, C=23.6, H=2.2, N=15.3, S=35.1, F=0% $Nb(NCS)_3O.OEt_2$ requires Nb=26.0, C=23.5, H=2.8, N=11.3, S=2.69, F=0%. I.R. absorptions of the solid were similar to those found in the last experiment.

c) To 5.3 m.moles TaF_5 and 20 m moles Et_2O were added approximately 17 m. moles of Me_3SiNCS. The mixture separated into a heavy, viscous orange layer and an orange solution composed chiefly of Me_3SiF and Et_2O. An attempt to follow the reaction by 19 F N.M.R. spectroscopy at 20°C failed because of the heat generated by the reaction. At lower temperatures the viscous layer froze out. The viscous orange layer, when all the volatiles were pumped off, gave the analysis C=15.6, H=2.4, S=15.6, F=2.4%. $Ta(NCS)_4F.Et_2O$ requires C=19.6, H=2.1 S=26.1 F=3.9% The orange material gave the following I.R. and Raman bands (all frequencies in cm^{-1}, Raman intensities in brackets) I.R. 3020w, 2985s, 2935m, 2915w, 2218m, 2186m, 1970-2000, vvs,vb, 1469m, 1444ms, 1385s, 1317m, 1276w, 1254m, 1186ms, 1144ms, 1083s, 995s,b, 937m, 873s, 848sh, 825sh, 795s,b, 750s,b, 615s, 498s. Raman, 195w, 350 (220) polarised, halfwidth= 60 cm^{-1}. 502(40) polarised, 620(20),b, 1450(10), 1890(10), 1947(10), 2029(120), polarised, half-width = 40 cm^{-1}. The Raman spectra showed other broad, polarised bands, but these were not easy to pick out.

Reactions of pentafluorides with Me_3SiNCO.

a) To 4.6 m.moles NbF_5 were added 15 m.moles Et_2O and 30 m.moles Me_3SiNCO. The mixture reacted over several hours to give a fine purple-black powder. The material gave the analysis Nb=32.2, C=17.6, H=1.2, N=15.7, F=8.4%. $NbF(NCO)_4$ requires Nb=33.7, C=17.4, H=0, N=18.5, F=6.9%. $NbF_2(NCO)_3.OEt_2$ requires Nb=28.1, C=25.4, H=3.0, N=12.7, F=11.5%. The solid gave the following I.R. absorptions (all frequencies in cm^{-1}) 3560mw, 2160vs, asy, 1398m, 1220w, 1090mw, 1005m,b, 880w, 795w, 760w, 665m,b, 612s.

The material did not look pure and washing a portion with CH_3CN did not improve its appearance. The portion washed in CH_3CN did not melt below 360°C, was soluble in EtOH, gave a white precipitate with water, and developed an acrid smell when left in air.

b) To 6.4 m.moles TaF_5 were added 11m.moles Et_2O and 34 m.moles Me_3SiNCO. The mixture did not appear to react at all for two days, despite heating to 70°C for an hour. A cream-white precipitate formed in the third day and after this the reaction behaved as if it was auto-catalytic. After three days the precipitate was washed with the liquids present and pumped dry. It gave the analysis C=17.0, H=2.3, N=7.8, F 0.5%. $Ta(NCO)_5$ requires C=15.4, H=0, N=17.9, F=0%. The I.R. spectra of the material was not good but showed the following absorptions (all frequencies in cm^{-1}) 3595m, 2210vb,vs, 1405ms, 1259ms, 1240w,

1188w, 1148w, 1088w, 1010w, 949m,b, 850s, [illegible]sy, 825m, 706m, 619s, 590w, 480b,vs. The cream powder was soluble in EtOH and ^{1}HN.M.R. of the solutions showed inequivalent Et groups. The solid gave a white precipitate with water.

Reaction of NbF_5+$(Me_3Si)_2O$.

Approximately 10 m.moles NbF_5 and a large excess of $(Me_3Si)_2O$ were mixed in a glass vessel and heated to 140°C for one hour. The I.R. spectrum of the volatiles showed the presence of $(Me_3Si)_2O$, Me_3SiF, and a little SiF_4. The white solid produced gave the analysis Nb=55.9 F=34.7% $NbOF_3$ requires Nb=56.0, F=34.4% The solid was shown to be amorphous by x-ray powder photography and gave only the following very broad I.R. absorptions (frequencies in cm^{-1}) 950 m, 650 vs, 450 m. The solid was light-sensitive and became royal blue when exposed to sunlight.

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CHAPTER III

^{93}Nb n.q.r. Investigations of some Niobium Compounds

Chapter III

Introduction

The results given and discussed in this chapter include the n.q.r. spectra of $NbF_5 \cdot XeF_2$, $Nb_2F_{10} \cdot XeF_2$, NbF_5, and the complexes of NbF_5 with Me_2O, Me_2S, CH_2ClCN, and pyridine.

As n.q.r. spectroscopy is a relatively new and obscure technique a short introduction to the principles involved will be given before proceding to discussion of the results. Symbols used in this chapter are listed in tables 3:1:1. As all theoretical predictions made are concerned with ratios of transitions energies rather than their absolute values almost all units have, for the sake of simplicity, been ignored in this presentation of the theory of n.q.r. spectroscopy. For a fuller discussion the reader is referred to references 1,2,3, and 4.

When the spin, I, of an atomic nucleus is greater than $\frac{1}{2}$ its distribution of positive charge is non-spherical and may be presented as an ellipsoid that is either oblate, or prolate with respect to the spin axis.

Table 3:1:1

Symbols used in this chapter

e= protonic change.

Q= scalar quadrupole moment of the nucleus.

q= $\psi_e \frac{3\cos^2 -1}{r_e} \psi^*_e \, d$ = field gradient at the nucleus

η= asymmetry parameter

m= magnetic quantum number of the nucleus.

I= nuclear spin

V= electrostatic potential at the nucleus

V_{ii}= gradient of V in the i^{th} dimension

n_o= occupation factor for niobium valence orbitals directed towards oxygen.

$n_{Fe}, n_{Fa}, n_{Fb}, n_{Ft}$ = occupation factors for niobium valence orbitals directed towards equatorical fluorine, axial fluorine, bridging fluorine and terminal fluorine atoms respectively.

K= constant

r_i= average distance of the electron i from the nucleus

$\langle r_i^3 \rangle_{av}$= average of r_i^3

$\hbar$ = Plancks constant $/ 2\pi$

(figs 1a,1b)

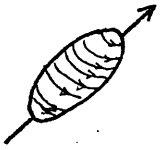


fig 1a

prolate nucleus

eQ > 0

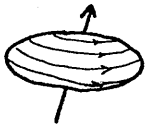


fig 1b

oblate nucleus

eQ < 0

The nucleus has an electric quadrupole moment, e Q, which is a measure of the deviation from spherical distribution of positive charge. Such a nucleus, when situated in an inhomogeneous electric field, has a potential energy dependent upon:- (a) the size of the field gradient, e.q; (b) the size of the quadrupole moment of the nucleus, e Q;

(c) the orientation of the quadrupole with respect to the field gradient, that is the nuclear magnetic quantum number, m.

If the electric field gradient is described by a symmetric tensor with diagonal elements V_{xx}, V_{yy}, V_{zz} such that $|V_{xx}| \leqslant |V_{yy}| \leqslant |V_{zz}|$ then

$$eq = V_{zz}$$

Because of the Laplace equation, ($V_{xx}+V_{yy} + V_{zz} = 0$) if we define another quantity, η, such that

$$\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$$

the field gradient tensor can be represented in terms of η and eq. x,y and z are known as the PRINCIPAL AXES. η is known as the ASYMMETRY PARAMETER and varies between 0, in environments of fairly high symmetry, and up to 1 in environments of low symmetry, (e.g. for Nb in rhombohedral $KNbO_3$ $\eta=0$ [5] In K $Cu(CN)_2$ where copper is three coordinate and almost planar with two strong Cu-C bonds and a weak Cu-N bond, C^1-Cu-C^2=134.2°, C^1-Cu -N=112°, C^2-Cu-N=108° [7] η for Cu is 0.78 [6].

Most nuclei with quadrupole moments have odd spin-values and for these nuclei the levels with m= ±I, ±I-1 ..... ±½ are degenerate in the absence of an applied magnetic field (ref 1,p36-37). Thus a nucleus with spin 3/2 e.g. ^{35}Cl, ^{119}Sn placed in a field gradient gives one observable transition between states with m= ½ and m= 3/2 with energy $\frac{e^2 q Q}{2\hbar}(1-\eta^{2/3})^{\frac{1}{2}}$ (2) In this case it is not possible to determine $e^2 q Q$ without perturbation of the nucleus by an applied magnetic field.

For ^{93}Nb, and other systems with spin 9/2, the secular equations for the quadrupole splittings of nuclear energy levels have been solved in terms of $e^2 q Q$, and the solutions tabulated [8,9] The variations of the energy levels with η in units of $\frac{1}{24} e^2 q Q$ are shown diagramatically in Fig 3:1:2. The energies of transitions between levels thus vary as shown in fig 3:1:3 (see also appendix 4), and the ratios of observed

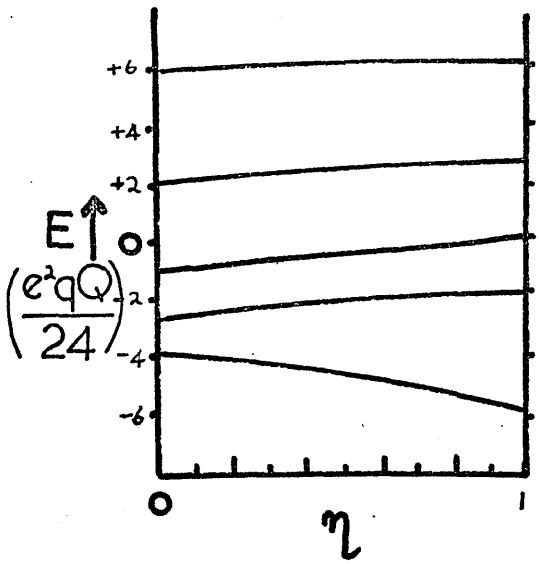


Fig 3:1:2 Variation of ^{93}Nb Energy levels with changing η

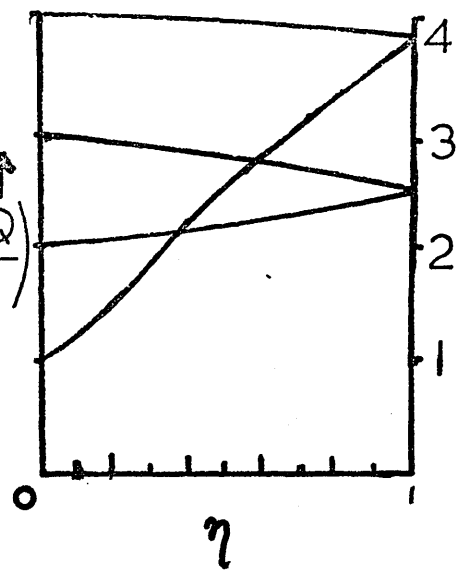


Fig 3:1:3 Variation of energies of nuclear quadrupole transitions of ^{93}Nb with changing η

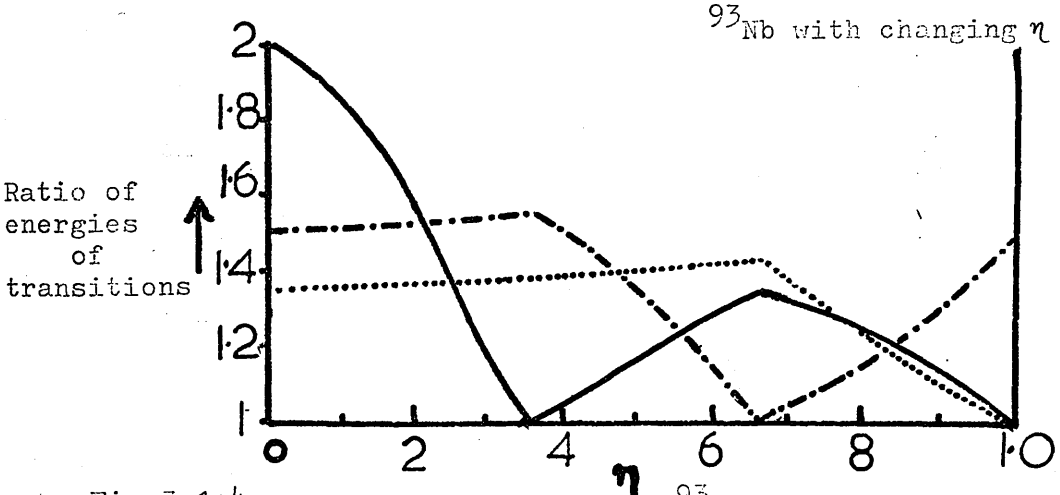


Fig 3:1;4 Variation of ratios of ^{93}Nb transitions with changing η

——— = ratio of two transitions of lowest energy
-·-·- = ratio of two transitions of intermediate energy
····· = ratio of two transitions of highest energy

transitions vary as shown in fig 3:1:4. Using graphs of these types the experimental ratios of observed frequencies may be used to calculate η and hence $e^2 q Q$.

The main contributions to eq at the nucleus in a species with no unpaired electrons, such as niobium(V) are:- (10,11)

a) valence electrons associated with the chemical bonding and having a high probability of being found near the nucleus,

b) electrons and nuclei present in atoms surrounding the central niobium atom,

c) Polarisation of the inner shells of electrons on the niobium atom by surrounding atoms.

Of these factors the largest is the first and this alone will be considered in detail. (Sternheimer Shielding, (12) which involves polarisation of the inner shells of electrons by the outer electrons, will not be considered)

A "point" or "donated" charge model has been developed (11,13) to predict eq, and η, in terms of the number of electrons, n_i, in each of the valence orbitals of the central atom. A given number of electrons, n_i, in an orbital, directed at angle θ to a principal axis j, is considered to give the contribution

$$V_{jj(i)} = K\, n_i \left(\frac{3\cos^2\theta - 1}{\langle r^3 \rangle_{av}}\right)$$

to the gradient of electrostatic potential along the J axis,

TABLE 3:1:2

Contributions of niobium valence electrons to the field gradient at the niobium nucleus.

atom	axis	$3\cos^2\theta-1$	contribution to V_{ii}	V_{ii}
O	Z	2	$-2n_o$	$2(n_{Ft}-n_o)$
$4F_e$	Z	-1	$+4n_{Ft}$	
Fa	Z	2	$-2n_{Ft}$	
O	X	-1	$+n_o$	$-(n_{Ft}-n_o)$
$2F_e(x)$	X	2	$-4n_{Ft}$	
$2F_e(y)$	X	-1	$+2n_{Ft}$	
F_a	X	-1	$+n_{Ft}$	
O	Y	-1	$+n_o$	$-(n_{Ft}-n_o)$
$2F_e(y)$	Y	2	$-4n_{Ft}$	
$2F_e(x)$	Y	-1	$+2n_{Ft}$	
F_a	Y	-1	$+n_{Ft}$	

where r is the distance between the electron and the nucleus. Where orbitals are of the same type, $\langle r_i^3 \rangle_{av}$ and the constant K are approximately the same in all cases, and will be left out of this discussion from now on.

To illustrate the use of this method the contribution of the valence electrons to the field gradient at the niobium nucleus in the pseudo-octahedral species of fig 3:1:5 are given in table 3:1:2

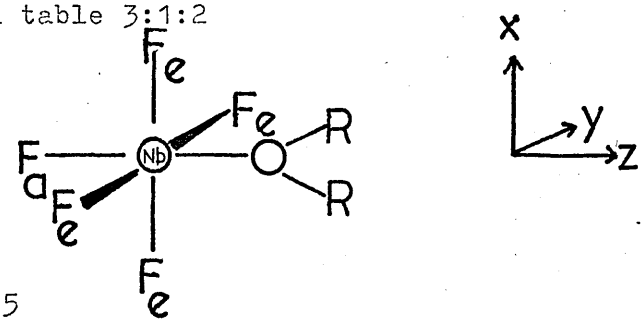


Fig 3:1:5

pseudo octahedral stereochemistry adopted by 1:1 pentafluoride adducts.

It may be noted that in table 3:1:1 the approximation is made that $n_a = n_e = n_t$. In view of the similarity of equatorial and axial metal-fluorine bond lengths in tetrameric NbF_5[14] (see fig I:1)this is reasonable.

The point charge model and its application entail a large number of approximations. The main justification for its use is that it is simple, and has been shown to work reasonably well[11,15,16,17] and to provide a method for differentiating between 4,5 and 6 coordination of the metal in compounds of iron and tin. It can also differentiate between the different isomers of compounds of the same coordination number,

e.g. cis and trans disubstituted octahedra [11,16,17].

Most reported work on quadrupole splittings of nuclei of central atoms has been by Mössbauer studies of ^{57}Fe, and ^{119}Sn in which quadrupole splittings, for nuclear transitions between a ground state, with spin $\frac{1}{2}$, and an excited state with spin 3/2, are observed. η, and hence $e^2 q Q$, is found from changes in the shape of Mössbauer absorption lines upon application of a magnetic field to the sample. Because of the difficulty of these magnetic experiments, the work on ^{119}Sn and ^{57}Fe systems has been largely based upon the observed quadrupole splittings.

N.Q.R. studies of ^{93}Nb systems have the great advantage that $e^2 q Q$, and η follow immediately from measurement of the observable transitions in the absence of a magnetic field, but suffer from the great disadvantage that, unlike the ^{119}Sn and ^{57}Fe systems, there have been virtually no studies on model compounds.

The field gradient around an atomic nucleus in a solid fluctuates with time because of thermal vibrations of the atoms in the crystal. The most important of the thermal vibrations are torsional modes whose frequencies are much higher than those of quadrupole resonance so that a time-average of the field gradient is observed. When the amplitudes of thermal vibrations increase the average field gradient becomes smaller.[18,19] Thus it would be expected that as

the temperature of a sample is decreased, and the mean amplitude of thermal vibration is decreased the observed frequencies should increase. This is known as the "Bayer Effect". In liquids, and solids where molecular rotation occurs with random orientation no quadrupole resonance can be observed because of broadening of resonance frequencies. N.Q.R. transitions are generally recorded at 77 K to minimise the Bayer effect.

Quadrupole resonance frequencies are known to change if pressure is applied to the sample (e.g. ref. 20). It seems likely [1] that the principal mechanism giving rise to pressure shifts, is the modification of the internal electric field caused by displacement of the molecules in the crystalline lattice. If pressure were applied non-uniformly the lines would be broadened and perhaps made undetectable. It has been shown that slow crystallisation of alkyl bromides and iodides gave samples with satisfactory n.q.r. spectra, whilst rapidly cooled samples gave no resonances [21] and strain may have been an important factor. The presence of impurities also leads to broadening [3] and this may also be due to strain.

Pressure effects can be related to changes in the volume of the crystal. Thermal expansion causes a volume change when the temperature is changed which leads to a change in observed resonance frequencies. This "volume

effect" may cause observed frequencies to increase, or decrease with increasing temperature (e.g. ref. 22).

Two types of behaviour can be envisaged for variation of resonance frequencies depending on whether the supplementary, Bayer, and volume terms complement, or oppose each other. (figs. 3:1:6, 3:1:7)

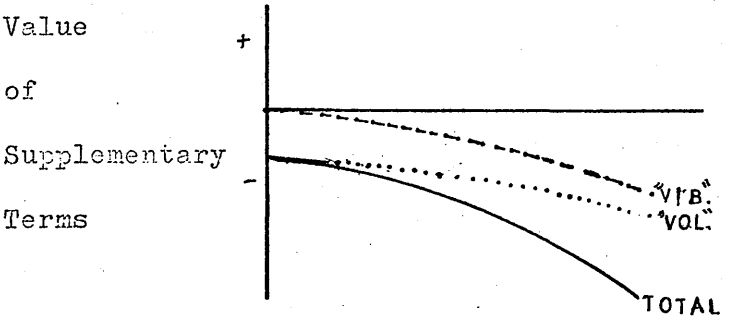


Figure 3:1:6 Supplementary contributions to field gradient complementing each other.

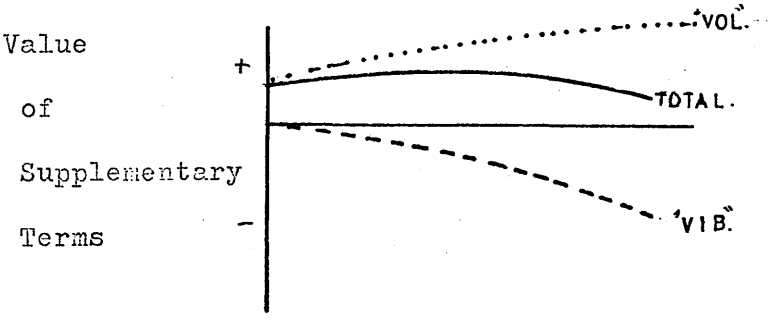


Figure 3:1:7 Supplementary contributions to field gradient opposing each other.

In a crystalline environment it is possible that chemically equivalent atoms will be crystallographically non-equivalent.

Because the crystalline field can be different from non-equivalent nuclei several different pure quadrupole frequencies may exist for each transition. The effect of crystalline field is generally less than 1% [13] of that due to valence shell electrons but may, in some cases, be up to 3% (e.g. in 1.3.5. trichlorobenzene. [23] It can be neglected in the investigation of the electronic structure of molecules, but it can be useful in detecting crystalline phase transitions, which produce an abrupt change in frequencies, and in some cases the number of frequencies observed.

Because of the lack of model compounds work presented in this chapter must be regarded, to some extent preliminary in its nature. It was chiefly aimed at elucidation of the structure of 1:1 and 1:2 adducts of niobium pentafluorides with organic bases, and xenon difuoride, and of substituted niobium pentafluorides.

It was also hoped that the work might provide a basis for determination of the structures of other niobium(V) compounds, and give some indication of trends of charge distribution within the compounds investigated. In complexes of gallium trichloride with organic bases, Tong [24] has found correlations between ^{69}Ga and ^{35}Cl, n.q.r. frequencies, and between n.q.r. frequencies and heats of complex formation. The ^{69}Ga frequencies were ten to twenty times as sensitive to change of ligand as were the ^{35}Cl

frequencies. It was felt that this work might yield a correlation between ^{93}Nb, n.q.r. frequencies and ^{19}F chemical shifts.

The 1:1 niobium pentafluoride-base complexes investigated here are thought to have a pseudo-octahedral structure (figs 3:1:5, 3:1:8b, also section 1:4). As discussed previously (section 1:4) the structures of the 1:2 pentafluoride-base complexes are unknown but a variety of seven-coordinate structures based upon pentagonal bipyramids (e.g. ReF_7[25], $UO_2F_5^{3-}$[26] figs 3:1:8 g-j) and the face centred trigonal prism (e.g. NbF_7^{2-}[27], fig 3:1:8 k) are possible. Ionic structures, involving a mixture of six, and eight coordinate ions (MF_6^-, $MF_4L_4^+$) have also been proposed[28]. Eight coordinate ions are mostly square antiprismatic, (e.g. TaF_8^{3-}[29]), dodecahedral (e.g. $Mo(CN)_8^{4-}$[30]) or cubic (see figures 3:1:8 l-r).

The dodecahedron, and square antiprism can be defined by the angles between the bonds and the S_4, and S_8 axes respectively. The angles used in the calculations for table 3:1:3 were based upon the predictions[32] of a "hard sphere model" (H.S. model) which minimises repulsion between non-bonded atoms, or a model maximising the angular dependent parts of the hybrid valence orbitals of the central atom (M.H. model).

All the basic 6-, 7-, and 8- coordination types discussed in this chapter are illustrated in figures 3:1:8 a-r along

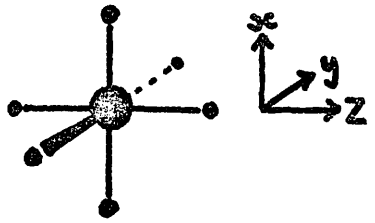
with the axis systems used in the point-charge calculations, for values of electron field gradient tensor components, and η, given in table 3:1:2. In $K_2NbF_7^{2-}$ the NbF_7^{2-} ion is distorted from C_2v symmetry.[27] Because of this, and difficulties in fixing the principal axis system for face centred trigonal prismatic ions no calculations have been made for these ions. The calculations are dependent upon the values of η, and hence $3\cos^2\theta - 1$, used. In NbF_5, and presumably other of these compounds, distortions from the ideal angles of the parent structure can be observed [14]. However, in view of the approximate nature of the point charge model, and difficulties arising, even in compounds of known structure, because the bonding orbitals are not always directed along inter-atomic lines (see e.g. ref (31).), no allowances were made for distortions in the calculations for table 3:1:3. $\frac{d}{d\theta}(3\cos^2\theta - 1) = -6\sin\theta\cos\theta$ which is 0 when $\theta = 0$, or 90° and 3 when $\theta = 45^\circ$, so that in many cases, (e.g. fig 3:1:8b, table 3:1:2) quite large distortions will have very little effect because θ is close to 0, or 90°.

TABLE 5:1:3

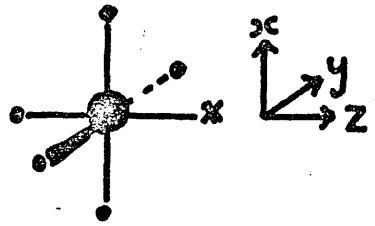
Electron Field Gradient tensor components for Nuclei in various environments.

Structure	V	η
a)	$V_{zz}=0$	0
b)	$v_{zz}=2n_F-2n_x$	0
c)	$-V_{zz}=2(n_F-n_x)$	0
d)	$V_{zz}=4n_F-4n_x$	0
e)	$V_{zz}=-(2n_F-n_{x'}-n_{x^2})$	0
f)	$V_{zz}=4n_F-2n_{x'}-2n_{x^2})$	0
g)	$V_{zz}=5n_F-4n_x$	0
h)	$V_{ii}=2n_F-n_x$ $V_{ii}=2n_x-2.5n_F$ $V_{kk}=0.5n_F-n_x$	?
i)	$V_{ii}=2n_x-n_F$ $V_{jj}=-0.43n_F-0.07n_x$ $V_{kk}=1.43n_F-1.93n_x$	?
j)	$V_{ii}=2n_x-n_F$ $V_{jj}=2.93n_F-3.43n_x$ $V_{kk}=1,43n_x-1.93n_F$	?
l)	$V_{zz}=3.68n_a-2.52n_b$ $\theta_A=56.9^o$ $\theta_B=69.5^o$	0
l)	$V_{zz}=4.01n_a-3.04n_b$ $A=35.2^o$, $B=73.5^o$	

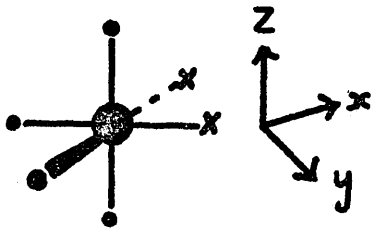
Structure	V	η
m) $\theta_A=59.25^o$	$V_{zz}=1.76n_f$	0
m) $\theta_A=57.3^o$	$V_{zz}=0.96n_F$	0
n) $\theta_F=\theta_x=57.3^o$	$V_{zz}=0.48(n_F+n_x)$	0 0
n) $\theta_F=\theta_x=59.25^o$	$V_{zz}=0.88(n_F+n_x$	0
n) $\theta_F=59.25^o$, $\theta_x=57.3^o$	$V_{zz}=0.88n_F-0.48n_x$	0
p) $\theta_F=59.25$ $\theta_x=$ F	$V_{ii}=0.88(n_F+n_x)$ $V_{jj}=1.78n_F-2.66n_x$ $V_{kk}=1.78n_x-2$	?
p) $\theta_F=57.3$	$V_{ii}=0.48(n_F-n_x)$ $V_{jj}=1.88n_F-2.36n_x$	?
p) $\theta_F=59.25^o$ $\theta_x=57.3^o$	$V_{ii}=0.88n_F+0.48n_x$ $V_{jj}=1.78n_F-2.36n_x$ $V_{kk}=1.88n_x-2.66n_F$	?
q,r,	$V_{zz}=0$	



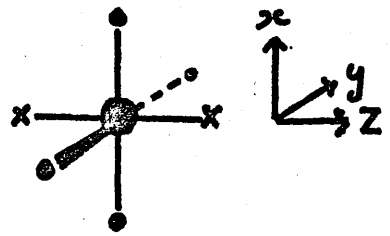
a) O_h Symmetrical octahedron e.g. NbF_6^-



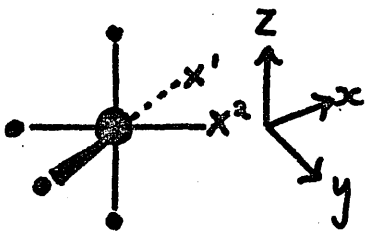
b) C_{4v} Substituted octahedron e.g. $NbF_5.OR_2$., NbF_5-F.XeF



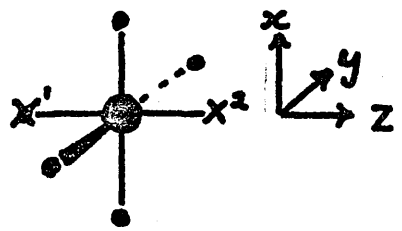
c) C_{2v} symmetrically cis disubstituted octahedron e.g. NbF_5 (14)



d) D_{4h} symmetrically trans disubstituted octahedron

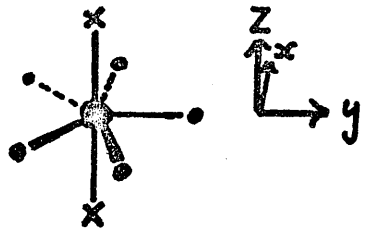


e) C_s asymmetrically cis disubstituted octahedron (e.g. the Sb atom closest to Xenon in $XeF_2.2SbF_5$ (35))

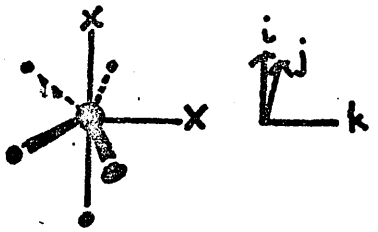


f) C_{4v} asymmetrically trans disubstituted octahedron

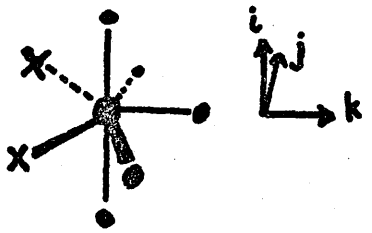
Fig 3:1:8 (a-f)



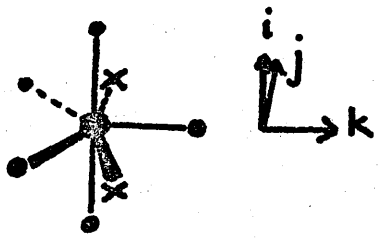
g) D_{5h} trans disubstituted pentagonal bipyramid (e.g. $uO_2F_5^{3-(26)}$)



h) C_s cis disubstituted pentagonal bipyramid

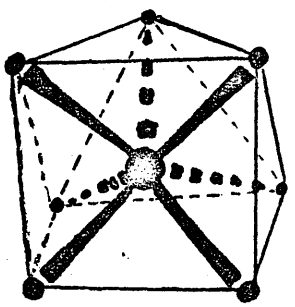


i)

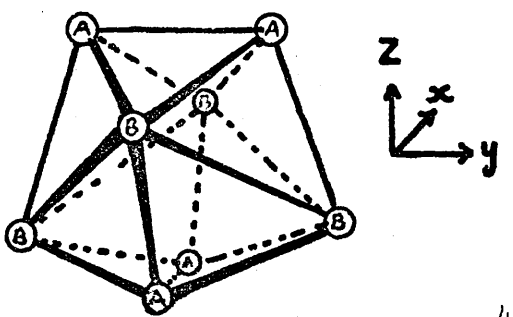


j)

C_{2v} disubstituted pentagonal bipyramids

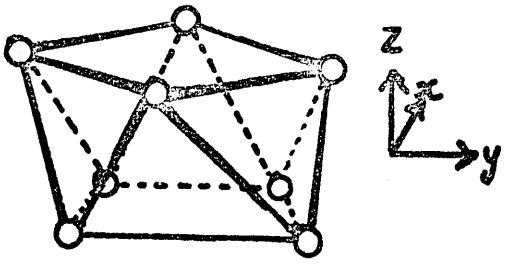


k) Face-centred tigonal prims, e.g. $NbF_7^{2-(27)}$

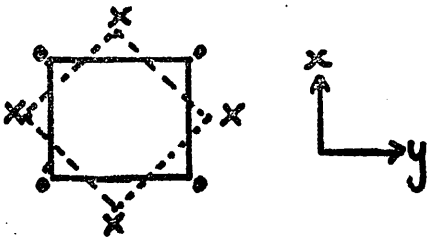


l) Dodecahedron e.g. $Mo(CN)_8^{4-(30)}$

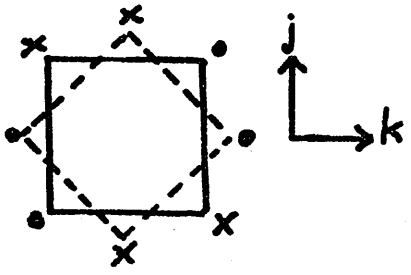
Fig 3:1:8 (g-l)



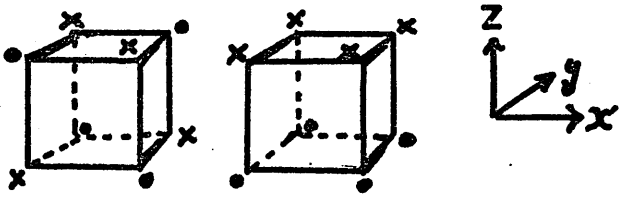
m) Square antiprism
e.g. TaF_8^{3-}(29)



n) C_{4v} tetra substituted square antiprism



p) C_{2v} tetra substituted square antiprism



q),r) cubes

Fig 3:1:8 (m-r)

For the sake of clarity the stuctures k-r are represented by polyhedra defined by the ligands rather than by the bonds to the central atom.

The H.S. model gives $\theta_A=36.9^\circ$, $\theta_B=69.5^\circ$ for the dodecahedron and $\theta=59.25^\circ$ for the square antiprism.

The M.M. model gives $\theta_A=35.2^\circ$, $\theta_B=73.5^\circ$ for the dodecahedron and $\theta=57.3^\circ$ for the square antiprism.

3:2 Results

$NbF_5.OEt_2$, NbF_5+SEt_2, NbF_5+SeEt_2, NbF_5Me_2SO, NbF_5 Anisole, $NbF_5.CH_3CN$, $NbF_5.CH_3CN$ in the presence of excess CH_3CN, $NbF_5.CH_3CH_2CN$, $NbCl_5.SMe_2$, $NbCl_5.CH_3CN$, and $Nb(OEt)_5$ all failed to give any observable resonance between 5 and 35 MHz at either room temperature, or 77 K. $NbF_5.(Me_2SO)_2$, $NbF_3.(NEt_2)_2.Py$, $NbF_4.NEt_2$, and $NbF_5.(Me_2SO)_2$ all failed to give any observable resonance between 5 and 55MHz at either room temperature, or 77 K. Observed n.q.r. spectra are given, along with experimentally calculated values of e^2qQ and η in tables 3:2:1-7.

TABLE 3:2:1

N.Q.R. Parameters of NbF_5

Temp °K group	trans-ition	E MHz	ratio	η	e^2qQ MHz
77 group one	9/2-7/2	19.478*	1.3396	0.204±.03	117.28 ±.24
	7/2-5/2	14.54			
	5/2-3/2	n.o.			
77 group two	9/2-7/2	19.057*	1.3411	0.23 ±.04	114.69 0.3
	7/2-5/2	14.21			
	5/2-3/2	n.o.			
273 group one	9/2-7/2	19.270*	1.3355	0.135±.02	115.80 ±.026
	7/2-5/2	14.429	1.526	0.130±.015*	
	5/2-3/2	9.458	1.659	0.140±.02	
	3/2-1/2	5.70?			
273 group two	9/2-7/2	19.002*	1.334	0.175±.02	114.29 ±0.05
	7/2-5/2	14.208	1.540	0.172*±.015	
	5/2-3/2	9.237	1.60	0.160±.02	
	3/2-1/2	5.70?			

* These values were used for calculation of e^2qQ

"groups" of resonances may be attributed to Nb nuclei in the same environment

TABLE 5:2:2

Temperature dependence of ^{93}Nb 9/2-7/2 transitions in Nb_4F_{20}

Temp. °K	E MHz	Temp. °K	E MHz	Temp. °K	E MHz	Temp. °K	E MHz
82	19.055	197	19.065	268	19.022	190	19.426
82	19.056	201	19.062	269	19.019	193	19.411
86	19.054	204	19.060	272	19.017	197	19.407
87	19.057	209	19.056	274	19.013	201	19.396
92	19.058	212	19.055	275	19.014	205	19.391
99	19.062	217	19.055			213	19.384
108	19.067	221	19.053	73	19.476	219	19.375
115	19.067	224	19.051	73	19.472	223	19.358
123	19.068	227	19.049	79	19.480	229	19.357
126	19.069	231	19.047	84	19.472	231	19.354
132	19.071	235	19.047	86	19.479	234	19.345
135	19.068	238	19.045	99	19.478	238	19.346
139	19.070	240	19.044	108	19.491	241	19.336
144	19.070	243	19.042	117	19.502	244	19.330
147	19.076	245	19.040	122	19.495	246	19.326
151	19.070	248	19.038	130	19.489	249	19.322
156	19.069	250	19.035	135	19.478	252	19.318
161	19.069	254	19.033	139	19.475	254	19.311
169	19.070	255	19.031	146	19.470	257	19.305
173	19.069	258	19.029	154	19.462	260	19.297
182	19.068	260	19.026	162	19.460	263	19.294
186	19.066	264	19.025	169	19.448	266	19.289
192	19.066	265	19.024	174	19.438	268	19.285
				181	19.426	271	19.283

TABLE 3:2:3

N.Q.R. Parameters of 1:1 NbF_5 complexes with Lewis bases.

Temp °K Group	trans-ition	E MHz	ratio	η	e^2qQ MHz
$NbF_5.Me_2O$					
77 group one	9/2-7/2	14.212	1.331	0.0±.06	86.19 ±.08
	7/2-5/2	10.603*	1.5028	0.02±.03*	
	5/2-3/2	7.047			
77 group two	9/2-7/2	14.138*	1.340	0.2±.2	84.86 ±.05
	7/2-5/2	10.603	1.5046	0.04±.05*	
	5/2-3/2	7.047			
273	9/2-7/2	14.359	1.331	0.0±.06	86.19 ±.08
	7/2-5/2	10.768*	1.5028	0.02±.03*	
	5/2-3/2	7.165			
$NbF_5.CH_2ClCN$					
77	9/2-7/2	16.63*	1.33	0.0±0.1	99.78 ±.20
	7/2-5/2	12.551	1.56?	0.24?	
	5/2-3/2	8.05?			
273	9/2-7/2	16.814*	1.333	0.00±.04	100.92. ±.07
	7/2-5/2	12.618	1.507	0.04±.04*	
	5/2-3/2	8.375			

* these values were used for calculation of eq^2Q

TABLE 3:2:4

N.Q.R. Parameters of NbF_5.2Py.

temp ^oK	trans--ition	E MHz	ratio	η	e^2qQ MHz
77	9/2-7/2	16.02	1.33	0.0 ±.2	96.1 ±.5
	7/2-5/2	12.02			
	5/2-3/2	n.o.			
273	9/2-7/2	16.695*	1.3341	0.05±.06	100.33 ±.04
	7/2-5/2	12.514			
	5/2-3/2	8.254	1.5161	0.10±.01*	

* these values were used for calculation of e^2qQ

TABLE 3:2:5 N.Q.R. Spectra of products of reaction of NbF_5 & Me_2S

Temp°K group	trans-ition	E MHz	ratio	η	e^2qQ MHz
77	9/2-7/1	15.74*			
			1.334	0.08±0.1	99.5
group	7/2-5/2	11.80			
			1.509	0.06±.04*	±0.2
one	5/2-3/2	7.82			
77	9/2-7/2	15.44*			
			1.331	0.0±.4	92.7
group	7/2-5/2	11.6			
			1.512	0.1±.2*	±0.7
two	5/2-3/2	7.67			

Other resonances found			
Sample 1,293°K	15.36, 14.87,	11.14, 10.25,	7.44 MHz
Sample 2,293°K	not Scanned	11.23, 10.88	7.47 7.25
Sample 2,273°K	15.36, 14.88, 15.01, 14.695,	11.25, 11.015, 11.16, 10.89.	7.47, 7.37
Sample 2,250°K	15.23, 14.865, 15.05,	11.28, 10.91, 11.16, 10.17.	none found
Sample 2,227°K	15.24, 14.88, 15.04,	11.28, 10.92 11.17, 10.11.	none found
Sample 2,210°K	15.12, 14.98,	11.33; 10.93, 11.16	none found

TABLE 3:2:6

N.Q.R. Parameters of NbF_5-XeF_2 compounds

atom	temp°K group	trans-ition	E MHz	ratio	η	e^2qQ MHz
$.Nb_2F_{10}.XeF_2$						
Nb [a]	77 group one	9/2-7/2	18.621*	1.3357	0.11±.05*	111.85
		7/2-5/2	13.940	1.498	0 ±.07	±.10
		5/2-3/2	9.30+			
		3/2-1/2	n.o.			
Nb [a]	77 group two	9/2-7/2	18.208*	1.3354*	0.12±.03	109.38
		7/2-5/2	13.635	1.498	0 ±.13	±.11
		5/2-3/2	9.10+			
Nb [b]	77 group one	9/2-7/2	12.665*	1.336	0.14±.07	76.11
		7/2-5/2	.9.48+			±.18
		5/2-3/2	n.o.			
Nb [b]	77 group two	9/2-7/2	12.17*	1.337	0.17±.13	73.2
		7/2-5/2	9.10+			±.5
		5/2-3/2	n.o.			
Nb [a]	290	9/2-7/2	18.20	1.333	0.0±.15*	109.20
		7/2-5/2	13.65	1.50	0.0±.2	±.26
		5/2-3/2	9.1+			

atom	temp ^{o}K group	trans--ition	E MHz	ratio	η	e^2qQ MHz
Nb^b	290	9/2-7/2	12.185*			
		7/2-5/2	9.1	2.017	0.08±.03	73.15
		5/2-3/2	6.06			±.11
$\underline{NbF_5.XeF_2}$						
	77	9/2-7/2	5.70*	1.36	0.4 ±.4*	34.6
		7/2-5/2	4.2‡			±.8
	290	9/2-7/2	5.65*	1.35	0.3 ±.3*	34.2
		7/2-5/2	4.2‡			±.6

* These values were used for calculation of e^2qQ

\+ resonances over lapped with each other and spurious noise in this region and may not be accurate.

‡ These resonances have frequencies too low to be accurately deternined (see experimental)

a,b See fig

TABLE 3:2:7

Temperature dependance of ^{93}Nb 9/2 - 7/2 transitions in $Nb_2F_{10}\cdot XeF_2$

Temp °K	E MHz	Temp °K	E MHz	Temp °K	E MHz	Temp °K	E MHz
73	18.208	131	18.46	191	18.284	229	18.264
73	18.620	152	18.302	194	18.286	235	18.260
74	18.208	160	18.302	202	18.278	89	18.217
79	18.208	167	18.296	205	18.275	107	18.238
82	18.621	170	18.295	212	18.272	124	18.313
102	18.53	178	18.291	221	18.268	273	18.229
127	18.316	185	18.290	225	18.265		

3:3 Discussion

Disorder effects, detected by the absence of high angle scattering in the x-ray powder photographs (see chapters 1 and 2) are thought to be responsible for the absence of observable resonance in a large number of compounds used in this study. Disorders in packing of the layers of the crystal and orientation of the species present, and faulting and twinning of crystals are all possible. Most of the compounds which gave detectable resonances have low melting points and this may have been important in annealing the material. Disorder in a crystal lattice gives non-regular crystalline fields and distortion of molecules in the region of the disorder, as described in section 3:1

The observed n.q.r. spectrum of NbF_5 at 273 and 77 K (table 3:2:1) indicates that niobium atoms with two physically different environments are present. A weak peak at approximately 5.7 MHz. in the n.q.r. spectrum of NbF_5 is tentatively attributed to the 1/2- 3/2 transition, but it might be spurious. It is not essential to the arguments which follow.

NbF_5 crystallises in the $C2/m$ space group (No 12) with two tetrameric units in the crystallographic unit cell [14] (i.e. one per primitive, or bravais unit cell [33]). In each tetramer there are two niobium atoms with site symmetry C_2, (g sites) and two with site symmetry C_s, (i sites). No significant differences in chemical environment are

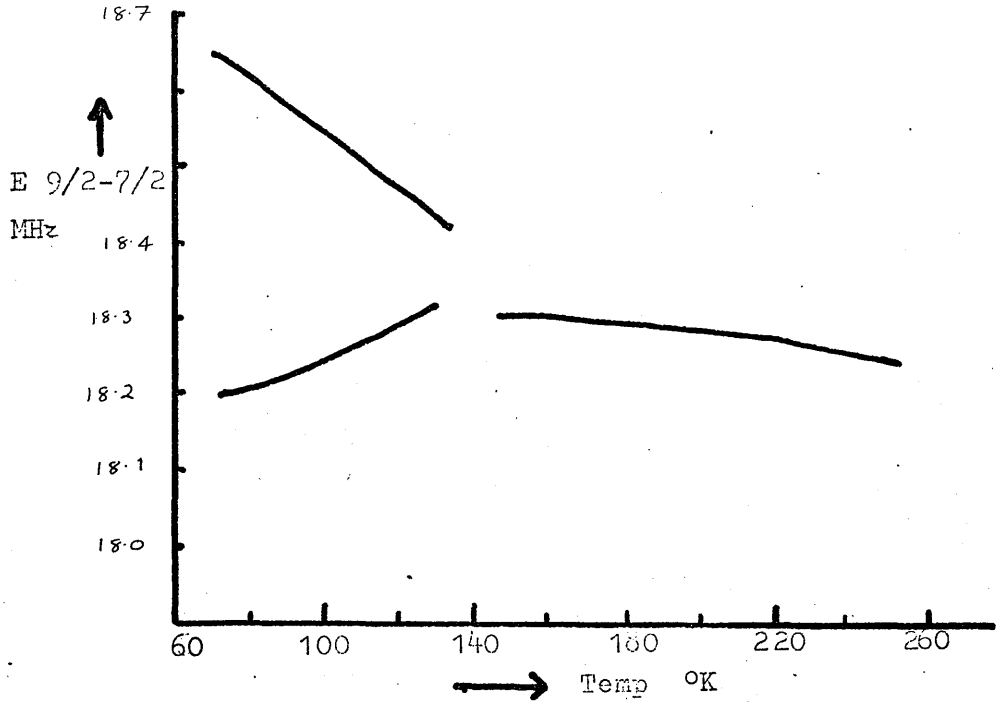


Fig. 3:3:2 Temperature dependence of 9/2 - 7/2 resonances of ^{93}Nb with highest value of e^2qQ in $XeF^+ \; Nb_2F_{11}^-$

detectable by x-ray single crystal techniques.[14] However, the differences found in $e^2q\,Q$ for the two environments ($\simeq$3% at 77 K) are rather large to be due to crystal fields alone[1,3] and this, with the marked difference in temperature dependence of $e^2q\,Q$ for the two environments, (see fig 3:3:1, table 3:2:2) indicates that the differences in environment, are due to a physical distortion of the chemical environment, rather than to crystal field, or vibrational effects. The deviation of η from the value of zero expected for a regular, cis disubstituted, octahedron (fig 3:1:8:c) is attributed to the observed distortion of bond angles from 90°[14]

The n.q.r. spectrum of $NbF_5.Me_2O$ at 77°K indicates two physical environments of ^{93}Nb atoms whilst that at 273 K indicates only one. (Table 3:2:3). It is concluded that a phase change occurs between these temperatures. The n.q.r. spectra of $NbF_5.Me_2O$, and $NbF_5.CH_2ClCN$ are consistent with the presence of pseudo-octahedral (C_{4v}) symmetry at the niobium atom. In this environment both distortion of bond angles from the "ideal" octahedral angles, and asymmetry of the base, might produce asymmetry in the electric field gradient tensor. In both complexes the experimental values of η are small, indicating that both effects are almost negligible.

The n.q.r. spectra of samples of "NbF_5+Me_2S" are not

consistent with the presence of a single compound, and cannot, except at 77 K, be arranged in groups corresponding to the four observable transitions. The spectrum at 77 K can reasonably be attributed to chemically similar ^{93}Nb atoms in physically different environments. As $NbF_5.Me_2S$ was probably a major component of the samples used the values of e^2qQ and η found are taken to be representative of the compounds.

The n.q.r. spectrum of the 1:2 complex, $NbF_5.2Py$ shows that only one physical and chemical environment has been detected and that in this environment $\eta = 0$. It is not possible to say which of its possible structures is taken up by $NbF_5.2Py$ on the basis of this information. It is unlikely to be one of those structures where η is not predicted to be zero (table 3:1:2, fig 3:1:8 structures h, i, j, p,).

In the n.q.r. spectrum of $XeF^+ Nb_2F_{11}^-$ resonances are found for ^{93}Nb in two, chemically different environments. The additional splitting at low temperatures, is attributed to crystallographic non-equivalence in chemically equivalent atoms because its size is consistent with this[13]. This phase change which occurs at 140 K (fig 3:3:2, table 3:2:7) is unlike normal phase changes[1,2,3] in that the observed frequencies do not change abruptly but appear to become equivalent as the temperature is raised. The temperature dependence

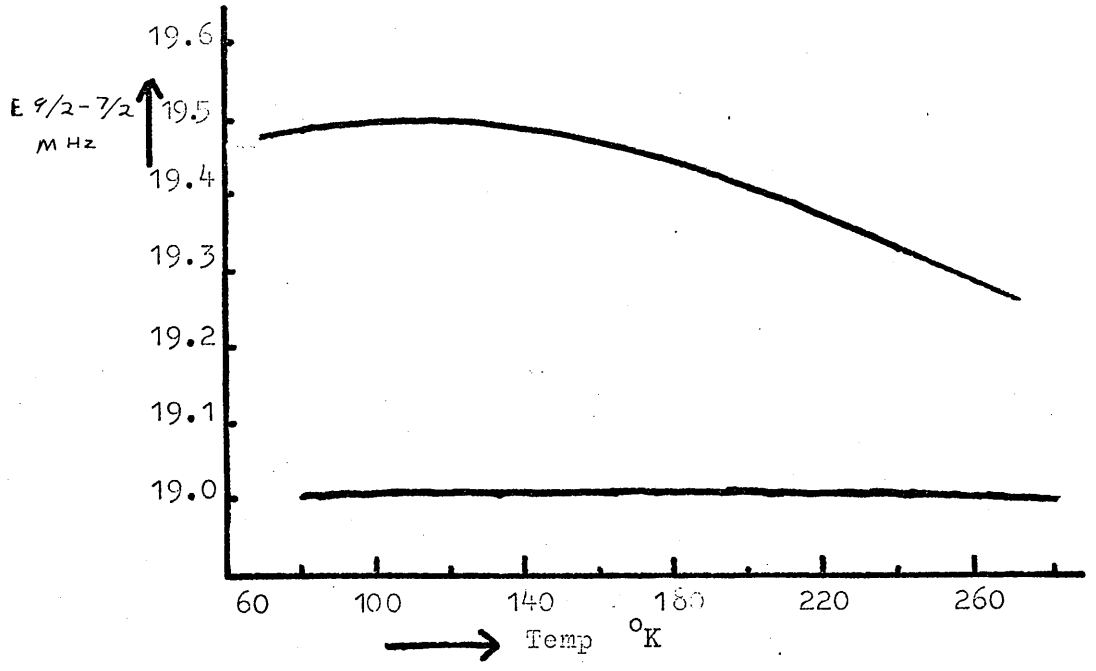


Fig 3:3:1 Temperature dependence of 9/2-7/2 resonances in NbF_5

of line energies below 140°K is far greater than expected if only external fields, or vibrational factors were involved (figs 3:3:1, 2, table 3:2:7) It is suggested that the observed behaviour is due to distortion of the molecules at low temperatures as the crystal dimensions change due to thermal expansion. Low-temperature x-ray diffraction studies of the compound might yield some interesting results.

The bonding in XeF^+-$M_2F_{11}^-$, and XeF^+ MF_6^- compounds has been a subject of some discussion, Raman spectra being taken as an indication that MF_6^-, or $M_2F_{11}^-$ and XeF^+ ions are present,(34) whilst the structure of XeF^+ $Sb_2F_{11}^-$ has shown an increase of the Sb-F bond length where the fluorine atom is directed towards Xenon(35) (see fig 3:3:3). Holloway (36) has suggested that the relative strength of the $F\underline{Xe^+\text{-}F}\cdots M$ and $Xe^+\cdots\underline{F\text{--}M}$ bonds are not always the same.

The NbF_6^- ion should give a quadrupole coupling constant of 0 MHz (table 3:1:2 structure a) The ^{93}Nb quadrupole coupling constant in $XeF^+.NbF_6^-$ (or $XeF_2.NbF_5$) (table 3:2:6) suggests a significant deviation from the purely ionic structure. The structure of $XeF^+.Nb_2F_{11}^-$ has not been determined but it may be assumed, by analogy with $XeF^+.Sb_2F_{11}^-$ that a unit approximating to $Nb_2F_{11}^-$ is present. In $XeF^+.Sb_2F_{11}^-$ the Xe-F-Sb bond is cis to the Sb-F-Sb bridge (see fig 3:3:3)

Calculations of the expected values of e^2qQ may be made using values of $n_F - n_{Fb}$, $n_F - n_{Fb'}$. ($n_{Fb'}$ ≡ orbital occupancy

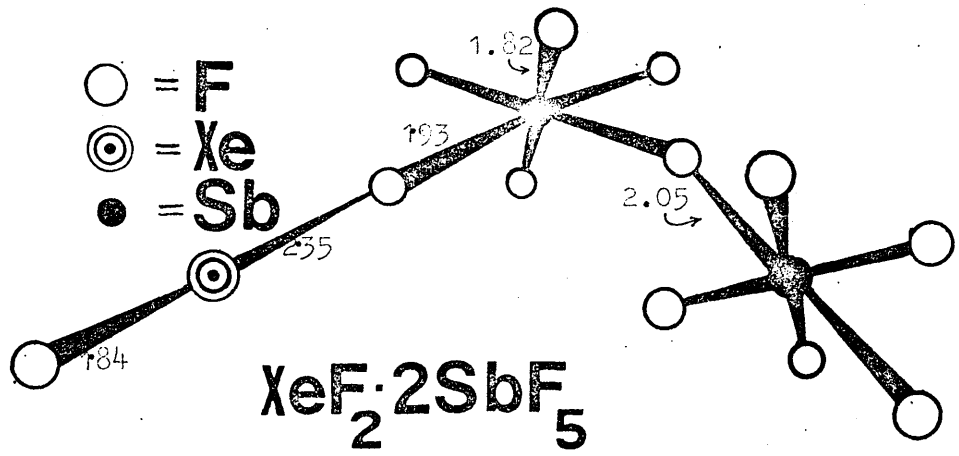
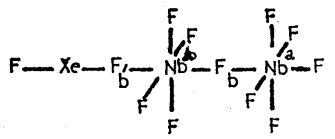
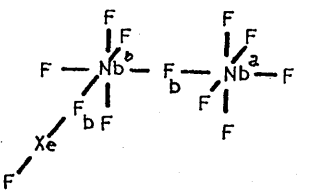


Fig 3:3:3

factor for Nb orbital directed towards F in the Xe-F-Nb bridge) derived from NbF_5 and $NbF_5.XeF_2$ and the predictions of table 3:1:2 (structures b,c,e,f.) Results for the two possible structures (1) and (2) are given below. (The superscripts a,b, refer to the Nb atoms as labelled in the diagrams; where crystal splittings were observed average values of e^2qQ are used)



Structure (1)



Structure (2)

NbF_5, 77 K.; $2n_F - 2n_{Fb}$ $e^2qQ = 116.0$MHz

$FXe\text{-}F\text{-}NbF_5$ 77 K; $2n_F - 2n_{Fb'}$, $e^2qQ = 34.4$ MHz

Structure (1) Nb^a; $e^2qQ = 2n_F - 2n_{Fb}$ 116.0MHz

Nb^b; $e^2qQ = 4n_F - 2n_{Fb} - 2n_{Fb'} =$ 150.4 MHz

Structure (2) Nb^a; $e^2qQ = 2n_F - 2n_{Fb} =$ 116.0MHz

Nb^b; $e^2qQ = 2n_F - n_{Fb} - n_{Fb'} =$ 75.2 MHz.

$XeF^+Nb_2F_{11}^-$ found at 77 K:-

Nb^1; $e^2qQ = 110.6$ MHz, Nb^2; $e^2qQ = 74.6$ MHz

The results are thus in excellent agreement with a cis structure and in future discussion it will be assumed that the structure of XeF^+ $Nb_2F_{11}^-$ approximates to structure (2)

It also follows from the predictions of table 3:1:2, and the experimental results that

$$\frac{n_F - n_{Fb'}\ (XeF_2.NbF_5)}{n_F - n_{Fb}(XeF_2.Nb_2F_{10};\ Nb^a)} = \frac{34.4}{110.6} = 0.31$$

$$\frac{n_F - n_{Fb'}\ (XeF_2.Nb_2F_{10}.Nb^b)}{n_F - n_{Fb}\ (XeF_2.Nb_2F_{10};\ Nb^a)} = \frac{2X74.6-110.6}{110.6} = \frac{39.2}{110.6}$$

$$= 0.35$$

Translating this into words - in $XeF^+.NbF_6^-$ the decrease in electron density in the Nb valence orbital directed towards fluorine when that fluorine is brought into contact with an XeF^+ species is 31% of that which occurs when the fluorine atom is bridge-bonded to another NbF_5 unit. In $XeF^+.Nb_2F_{11}^-$ the corresponding decrease in electron density in the orbital directed towards the fluorine directed towards Xenon is 35% of that in the orbital directed towards fluorine bridge-bonded to niobium. If the value $n_F - n_b = 116.0$MHz obtained from NbF_5 is used the decreases are 29.7, and 28.6% for $XeF^+.NbF_6^-$ and $XeF^+.Nb_2F_{11}^-$ respectively.

The Raman spectra of a series of $XeF_2.MF_5$ and $XeF_2.(MF_5)_2$ compounds have been studied and interpreted in terms of purely ionic structures.[34] Similar correlations may be made in these compounds (see table 3:3:1). The Raman spectra of $XeF_2.NbF_5$ does not compare very well with the spectra of previous $XeF_2.MF_5$ compounds [34] and this may have been due to reaction between the surface of the

sample and the pyrex sample tube. It was not possible to check this possibility because the sample consisted of one solid lump. However, because the sample was a solid lump it was unlikely that any impurities produced by surface reaction should have effected the observed n.q.r. spectrum.

TABLE 3:3:1

Raman Spectra of $XeF_2.MF_5$ compounds (frequencies in cm^{-1} intensities in brackets)

compounds	Xe-F ("XeF^+")	ν_1 MF_6^-	$\nu_2 MF_6^-$	$\nu_3 MF_6^-$
$Cs^+RuF_6^-$ (3+)		656(100)	581(18)	269(90)
$XeF^+RuF_6^-$(3+)	604(51) 599(86)	683(100)	645(48)	270(36) 260(18)
$Cs^+NbF_6^-$(40)		683(s)	562(w)	280(m)
$XeF^+NbF_6^-$	596(80)	769(3) 737(6)	663(4)	464(50)
$XeF^+Ru_2F_{11}^-$(3+)	604(100) 598(53)	$M_2F_{11}^-$ bands 733(18), 696 (23), 650(62) 285sh 716(97), 683 (54) 645(82) 269(58) 246(32)		
$XeF^+Nb_2F_{11}^-$	598(58)	766(13), 724(6) 680(3) 738(28) 712(4)		
$XeF^+Sb_2F_{11}$	618(50)	688(28) 650(24) 681(7) 525(10)		

3:4 Experimental

Highly specialised apparatus is required to observe nuclear quadrupole resonance. A comparison with N.M.R. spectroscopy is instructive. Most N.M.R. spectrometers consist, essentially of four parts,[37] a) a magnet to give a strong homogenous field to produce the non-degenerate energy levels for nuclear transitions b) a method for varying the magnetic field over a small range c) a radio-frequency oscillator of fixed frequency to produce a source of monochromatic electromagnetic radiation, and d) a radio frequency receiver to act as a detector and indicate when electromagnetic radiation is absorbed by the sample.

In n.q.r. spectroscopy the nuclear quadrupole interacts with a field gradient within the molecule and no static fields are normally needed. There can be no modulation of the field as in N.M.R. spectroscopy and frequency modulation must be used. The frequency range of n.q.r. is far greater than that of N.M.R., where shifts are seldom more than a few thousandths of the total applied frequency, and this presents certain experimental problems, but also means that meaningful results are obtained without the accurate frequency measurements of N.M.R. The Decca instrument[38] used in this work has a super-regenerative oscillator detector[39] with the range limitations 5-60 MHz and is considerably less sensitive in

in the lower ranges (5-10 MHz). A prototype of the Decca n.q.r. spectrometer was also available which gave spectra in the region 3.5-5 MHz if the "coherence" level was decreased. The frequencies registered in this region were not very accurate (0.1MHz)

$NbF_5.XeF_2$, and $Nb_2F_{10}.XeF_2$ were prepared by J. H. Holloway. (36) $Nb(OEt)_5$ was purchased from Alfa Chemicals. Preparation of other samples is dealt with in other chapters. The samples were loaded into 12.6 mm, thin walled pyrex tubes to a depth of between 1.5 and 2 cm in the inert atmosphere box and sealed under vacuum. The tubes were inserted into the coils which produced the r.f oscillating magnetic field. In all cases a combination of coils was used to scan the range 5-35 MHz; the 1:2 complexes and dialkylamido complexes were also scanned in the range 35-55 MHz. The time of scan per coil was 18 hours and the scan was recorded on a standard servoscribe recorder.

Sample temperatures were controlled by immersing the sample, rf coil, and sample chamber in a dewar flask filled with an appropriate fluid or slush bath. Variable temperature scans of $XeF_2.2NbF_5$, and NbF_5 were run by cooling sample chamber with liquid nitrogen and allowing them to warm to room temperature over a period of about twelve hours. Temperatures were measured by attaching a thermocouple to the sample chamber. The expected lag in temperature between sample and thermocouple was no more than $5^{\circ}K$.

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Appendix I

Experimental Methods

Because of the reactivity of higher metal halides many of the manipulations described in this thesis were carried out in vacuo, or in a Lintott inert atmosphere box. The vacuum line used was constructed with "Rotaflo" teflon-glass taps so that no grease was present in the line except between the liquid nitrogen "muck-traps" and the rotary pump. The vacuum was maintained with a three-stage mercury diffusion pump and an Edwards two-stage rotary pump and monitored using a Pirani gauge.

The Lintott inert atmosphere box was used to circulate oxygen-free nitrogen over activated molecular sieves and the water level in the box was monitored using an Elliot moisture monitor (model 111) fitted with a P_2O_5 electrolytic cell. The water level in the box was below 14 p.p.m. when it was used for transfer of hygroscopic materials. Readings from the monitor when the inert atmosphere box was dried with dishes of P_2O_5 suggests that the water level in a conventional dry box is between 80 and 300 p.p.m.

NbF_5, and TaF_5 were prepared in the apparatus shown in Figure A1:1 by passing a 10% F_2/N_2 mixture over heated

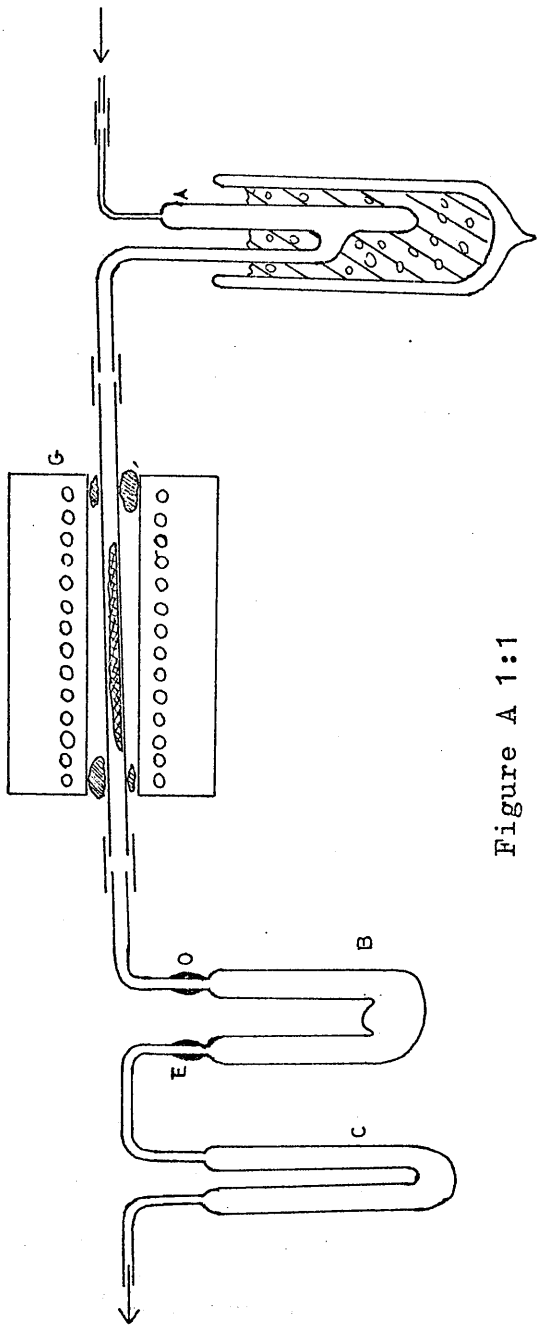
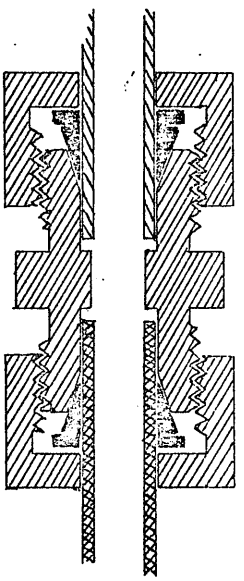


Figure A 1:1



Nb, or Ta. The apparatus was first degassed by flaming out, and passivated by passage of a 10% F_2/N_2 mixture for an hour. The fluorine, prepared by electrolysis of a KF/2HF melt, was dried in Trap A which was kept at -182°C with liquid oxygen. After passing fluorine for an hour the metal was heated with the furnace, G, to 250°C to initiate the reaction

$$M + 2\tfrac{1}{2}F_2 \rightarrow MF_5$$

after which the furnace was kept at 150°C. The pentafluoride condensed at the end of the metal reaction tube and was occasionally melted and collected in vessel B. When fluorination was finished the apparatus was purged of F_2 by passage of N_2 and evacuated. The vessel B was then sealed off at the constrictions O, and E.

MoF_5 was prepared by the action of MoF_6 on Mo at 150°C in a stainless steel, or monel "Hoke" bomb.

$$MoF_5 + Mo \rightarrow 6MoF_6$$

It was then sublimed from the tube into a glass vessel.

In the prep rations of pentafluoride, it is very difficult to avoid production of small amounts of oxyfluoride impurities. These pentafluorides were purified using the apparatus shown in figure A1:2. Pentafluoride was loaded into the Kel-F tube A in a Lintott inert atmosphere box

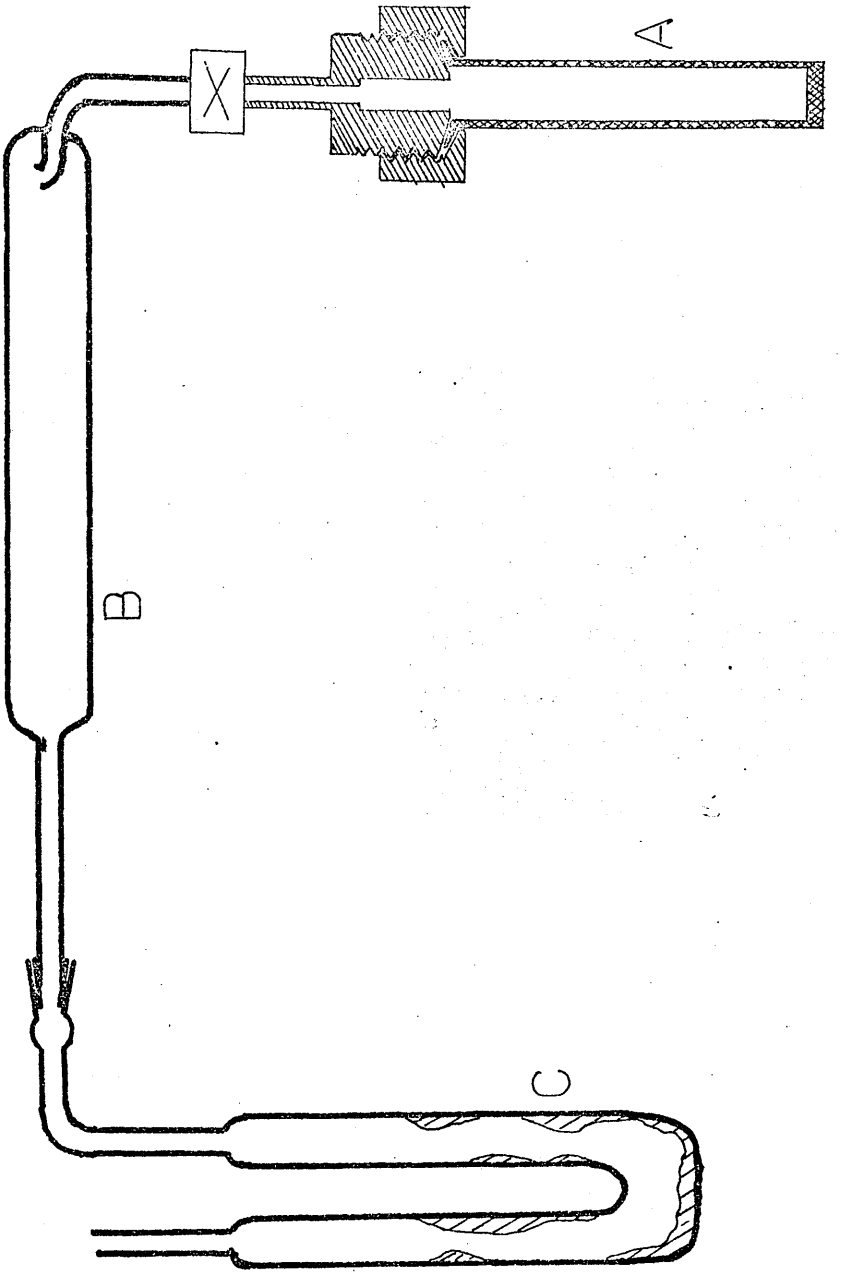


Figure A 1:2

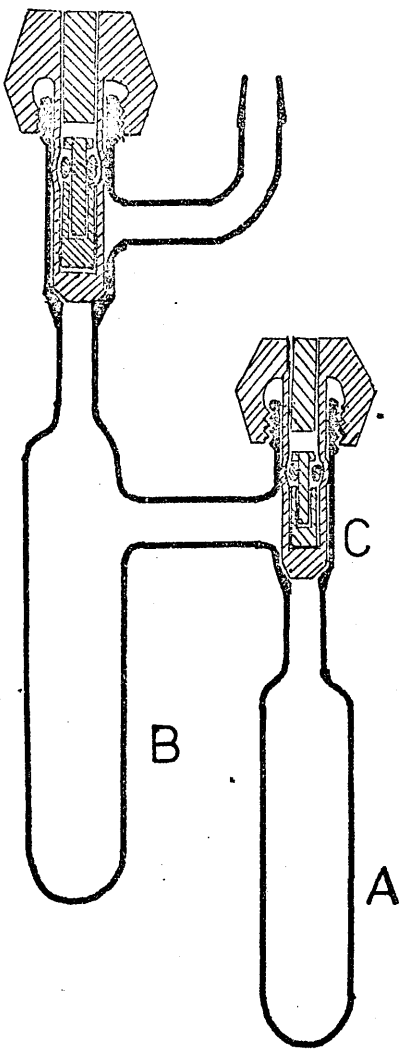
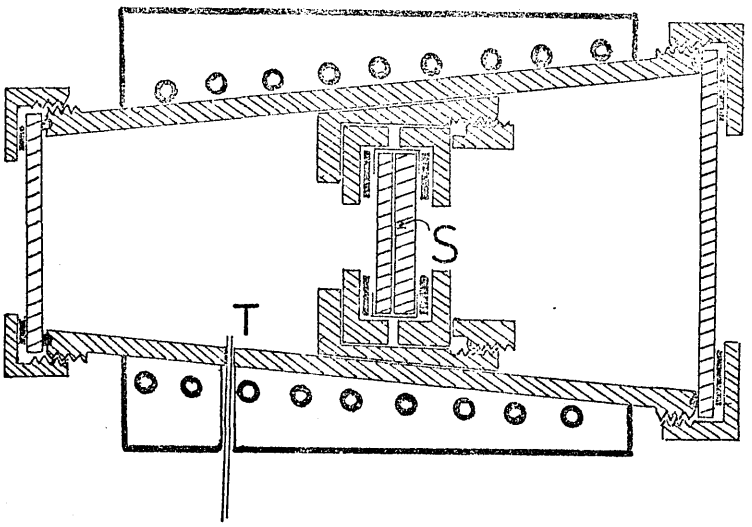


Figure A 1:3

and vacuum sublimed into a glass tube B. Because pentafluorides react with glass in the presence of traces of water it was necessary to thoroughly degas the vacuum line. To do this, fresh sodium was melted on the walls of trap C to act as a "getter" for any water present in the line. It is also present during sublimation to react with any HF absorbed by the pentafluoride during its preparation.

Reactions with the pentafluorides were carried out in vessels fitted with "Rotaflo" taps. In cas es where quantitative addition of reactants was required a two-compartment vessel (see fig. A1:3) was used. The vessel was evacuated, and reweighed. The other reagent was then put into compartment B and when the quantity was sufficiently adjusted the two materials were mixed. This vessel was also used for washing reaction products in vacuo. The solvent was added to the sample in vessel A and decanted into vessel B. Tap C can also be used as a crude filter.

The cells used for obtaining high, and low temperature I.R. spectra are shown diagramatically in figures A1:4 and A1:5 respectively. The high temperature cell was loaded with pentafluorides in the inert atmosphere box. There was about a ten minute time lag between temperatures at the thermocouple T and the sample S whilst the cell was heating.



Steel
AgCl
Teflon
KBr
Heaters

Figure A 1:4

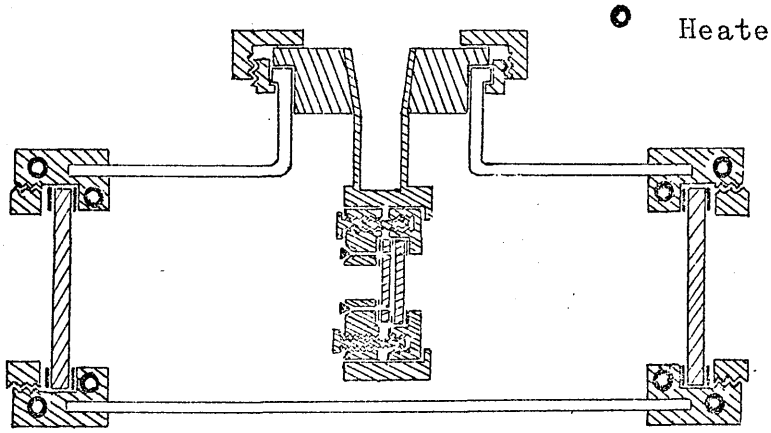


Figure A 1:5

Appendix II

Activity of I.R. and Raman modes in Pentafluoride Oligomers.

It was mentioned in Section 1:3 that an analysis had been made of the possible activities of bridging fluorine modes for some hypothetical MF_5 oligomers. The method used is illustrated for the hypothetical trimeric anion, with <u>trans</u> fluorine bridges, shown below

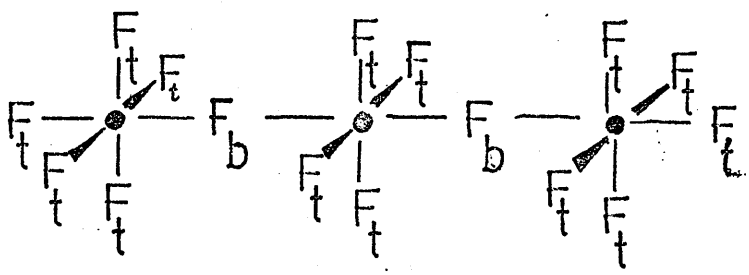


Figure A2:1

The numbers in table A2:1 are taken from the tables of Adams and Newton (ref. 70 Chapter 1) and represent the number of vibrational modes carrying the different group representations.

The characters of six orthogonal modes of the two bridging fluorine atoms (four of which are in two degenerate pairs, i.e. are "E" modes) are given in table A2:2. The "E" modes correspond to bending vibrations.

Table A2:1 Factor group analysis of an isolated $M_3F_{16}^-$ anion.

Atom	Sym.	Wyk. Site	No. of Atoms	Modes and representations									
				A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
Nb'	D_{4h}	A	1	0	0	0	0	0	0	1	0	0	1
Nb	C_{4v}	G	2	1	0	0	0	1	0	1	0	0	1
F_b	C_{4v}	G	2	1	0	0	0	1	0	1	0	0	1
F'	C_{4v}	G	2	1	0	0	0	1	0	1	0	0	1
F''	C_{2v}	J	4	1	1	1	1	1	0	1	1	0	2
F'''	C_S	S	8	2	1	2	1	3	1	2	1	2	3
Total modes				6	2	3	2	7	1	7	2	2	9
Translational modes				0	0	0	0	0	0	1	0	0	$2 \times \frac{1}{2}$
Rotational modes				0	1	0	0	$2 \times \frac{1}{2}$	0				
Total external modes				0	1	0	0	1	1	1	0	0	1
Total internal modes				6	1	3	2	6	1	6	2	2	8
I.R. active modes				0	0	0	0	0	0	6	0	0	8
Polarised Raman modes				6	0	3	0	0	0	0	0	0	0
Depolarised Raman modes				0	0	0	2	6	0	0	0	0	0

Table A2:2 Characters of the modes of vibration of bridging fluorine atoms in an $M_3F_{16}^-$ ion.

Vibrations of F_b*	x y z	→ →	→ ←	↑ ↑ ↗ ↗	↑ ↓ ↗ ↙
Characters of vibration	E	1	1	2	2
	$2C_4$	1	1	0	0
	C_2	1	1	-2	-2
	$2C_2'$	-1	1	0	0
	$2C_2''$	-1	1	0	0
	i	-1	1	-2	2
	$2S_4$	-1	1	0	0
	σ_h	-1	1	2	-2
	$2\sigma_v$	1	1	0	0
	$2\sigma_d$	1	1	0	0
Representation carried by vibration		A_{2u}	A_{ig}	E_u	E_g
Activity		I.R.	R.	I.R.	R.

* To visualise vibrations transpose arrows on to F_b in figure A2:1.

The representation carried by each mode is found by comparison of the characters of the mode with the character table for the C_{4v} group.

It may be shown that in all cases where linear fluorine bridging atoms are present there are movements of bridging fluorine atoms which correspond to formally active I.R. and Raman bands. There are other A_{1g} and A_{1u} modes and some mixing of the modes is inevitable. In particular, the A_{2u} modes must be mixed to produce translational modes, but as argued in section 1:3, this mixing has little effect on the energy of the modes.

Appendix III

Observed vibrational spectra, X-ray powder photograph data.

(All spectral frequencies are given in cm^{-1}, X-ray powder photograph data is given as the measured distance between arcs of scattered radiation (in cm) measured using Co Kα irradiation and a 114 mm camera. To convert to ^{o} divide by 0.4.)

TaF_5(solid) I.R.; 754 ms, 721vs, 698s, 674s, 667sh, 644ms, 585vw, 511b,s, 310w, 232sh, 216s,b, 187m, 138m.

Raman; 765(125), 754(25), 716(70), 673(5), 656(30), 267(50).

X-ray; 2.23vvw, 3.46_5w, 4.01w, 4.16_5w, 4.37m, 4.54s, 4.84_5vvw, 4.97w, 5.34_5ms, 5.44_5vw, 5.60_6vvw, 5.75_5vw, 5.98_5w, 6.21_5vw, 6.48mw, 6.67_5vw, 7.04vvw, 7.24vvw, 7.56m, 7.72_5vvw, 7.98mw, 8.47_5s, 8.67_5vw, 8.98s, 9.11_5w, 9.27vw, 9.46_5vvw, 9.65m, 9.76vvw, 9.93w, 10.28w, 19.49vvw, 10.58w, 10.79mw,d, 11.50m, 11.72vvw, 11.90vw, 12.00w, 12.35vw, 12.55_5mw, 12.79w, 12.92w, 13.16_5vw, 13.60vw, 13.97_5vw, 14.28vw, 14.69vw, 14.84w, 15.40w, 15.74w, 16.08mw.

NbF_5(solid) I.R.; 746s, 721vs, 700s, 692sh, 672s, 660s, 498s,b, 300m, 255sh, 235s, 213sh, 202vs, 170sh, 132s, 81m.

Raman; 756(120), 727(20), 697(50), 271(60), 237(20).

X-ray; 1.90vvw, 2.14vw, 3.48_5w, 3.95w, 4.14_5w, 4.29m, 4.46_5s, 4.87vw, 4.95vw, 5.31ms, 6.47w, 6.50w, 7.39mw, 7.97m, 8.65vw, 10.31vw, 10.58w, 10.85w, 11.38_5w, 11.89w, 12.48w, 12.71w.

MoF_5(solid I.R.; 763vs, 736ms, 722m, 710m, 696vs, 650b,sh, 150b,m, 307w, 250sh, 230s.

X-ray; 2.21w, 3.34_5w, 3.94_5vw, 4.13s, 4.46s, 4.87w, 5.02w, 5.31m, 5.47vw, 5.72w, 6.11vvw, 6.42w, 7.25w, 7.59vvw, 7.73vvw, 7.95w, 8.49w, 9.09m, 9.51vw, 9.76vw, 10.02vvw, 10.29mw, 11.70vw, 11.96d,vw.

$TaF_5 \cdot CH_3CN$, I.R.; 2327ms, 2301s, 2055w, 1030mw, 953m, 827w, 712vs, 655m, 612s,b, 410m, 300b,w, 260b,mw, 240, m.

Raman; 2300w, 710(30).

$TaF_5 \cdot CH_2ClCN$, I.R.; 3020m, 2324s, 1414m, 1266m, 950s, 903w, 750m, 715s, 669ms, 630m, 608vs, 521m, 240, m.

Raman; 2322(60), 746(20), 712(40), 673(30), 609(15).

$TaF_5 \cdot CH_3CH_2CN$, I.R.; 3300w, 3160w, 2296s, 2249w, 1415m, 1305m, 1075m, 860w, 783m, 708s, 657sh, 615vs, 570m, 410w, 300m,b, 240, ms.

$NbF_5 \cdot CH_3CN$, I.R.; 2320ms, 2298s, 2256w, 1367m, 1033m, 950m, 823w, 710b,s, 660b,s, 638b,s, 410m, 255m,sh, 240, m.

Raman; 2326(15), 2297(15), 705(90), 670(w), 590(4),

"$NbF_5 \cdot 2CH_3CN$" Raman 2322(3), 2293(2), 2250(3), 1366(3), 680(6), 640(8), 430(b,w), 390b,w, 2846b,w.

$NbF_5 \cdot CH_3CN$ X-ray; 2.78vw, 3.16vvs, 4.51vvs, 4.73vw, 4.98vw, 5.56m, 6.52_5vw, 6.76vw, 7.22_5mw, 7.92s, 9.23_5w, 9.55_5w, 9.85mw, 10.40_4w, 10.96w, 11.50vw, 11.98vw, 12.49w, 13.92vw, 14.39vw, 14.82vvw, 15.44vvw.

$NbF_5 \cdot CH_2ClCN$, I.R.; 3020m, 2320s, 2270w, 1414m, 1268m, 1191w, 948s, 903w, 750m, 719b,s, 660b,vs, 625b,vs, 520m, 387m, 300b, 240, vs.

Raman; 2317(7), 747(15), 714(12), 684(14).

$NbF_5 \cdot CH_3CH_2CN$, I.R.; 315ow, 2293vs, 2246w, 1418m, 1306m, 1250w, 1073m, 1000w, 856m, 820w, 784m, 704m, 640vvs,b, 568m, 290b,sh, 240, s.

Raman; 2295(10), 1470w, 1418w, 1311w, 1075(6), 1002(6), 863(w), 702(200), 668sh, 596(10), 568(10).

$MoF_5 \cdot CH_3CN$, I.R.; 2322m, 2397s, 2255w, (1028, 1015)mw, 953m, 720w, 703mw, 650b,vs, 635sh,b, 418w, 285b,m, 250,b, m.

Raman 2324(10), 2295(12), 955(6), 697(90), 665(5), 426(10).

$MoF_5 \cdot CH_2ClCN$, I.R.; 3010vs, 2960vs, 2312s, 1404s, 1264m, 1020mw, 948s, 893m, 752mw, 710m, 660b, vs, 630b,s, 522m, 330b,w, 240, m.

$TaF_5 \cdot OEt_2$, I.R.; 2295s, 2950w,sh, 2930w, 2880w, 1640w, 1476s, 1451ms, 1392s, 1360w, 1330m, 1287m, 1193s, 1152s, 1092s, 998vvs, asy, 880s, 834m, 880w, 778s, 695s,

650vs,sh, 618vvs, 512m, 475w, 350w, 260s,sh, 240, s.

Raman; 696(3).

$TaF_5 \cdot OMe_2$, I.R.; 1300w, 1264, 1155m, 1015b,m, (885, 875)m, 723ms, 710w, 670w, 630, 240, s.

Raman; 698(55).

$NbF_5 \cdot OEt_2$, I.R.; 2980ms, 2935m, 2870s, 2610w, 1975w, 1488s, 1445m, 1387s, 1322m, 1280m, 1188s, 1147m, 1108w, 1085s, 998vs,b,asy, 879vs, 828m, 791sh, 771s, 690vs,b, 640vvs,b, 506m, 467m. No spectra taken below 450 cm^{-1}.

$NbF_5 \cdot OMe_2$, I.R.; 3010sh, 2965vs, 2920vb,s, 2853vs, 2300w, 2020w, 1880b,w, 1258w, 1157m, 1020m,b, 970w, 882m,asy, 825b,w, 722m,w, 709m, 674sh, 666vs, 643sh,s, 595, 240, s.

Raman; 880(10) 690(200), 664(30), 593(7), 224(4). Raman intensities of this compound are unreliable because of its intensity.

$NbF_5 \cdot OMeC_6H_5$, I.R.; 3060m, 3020sh, 2950w, 2930mw, 2864mw, 1880w, 1630m, 1585b,m, 1510sh, 1490sh, 1478s, 1459sh, 1380w, 1335w, 1285mw, 1215b,vs, 1185sh, 1161s, 1120sh, 1111s, 1038w, 1017m, 938b,vs, 905sh, 815s, 786vw, 756s, 680-620vvs, 595sh,w, 490b,s, 380b,w, 300b,mw.

$TaF_5 \cdot (Me_2SO)_2$, I.R.; 3020m, 1440sh, 1419w, (1331,1324)w, (1314, 1308)vw, 1041m, 1028m, 1011sh, (1000, 995)s, 970ms, 946sh, 938b,s, 722m, 583s,asy, 570w, 550b,vs, 472m, 460sh, 359m, 331w, 310ms, 260m, 240, s.

Raman; 723(50), 691(140), 604(30).

X-ray; 2.83_5vvs, 3.10ws, 3.49vw, 3.69_5s, 4.26w, 4.66s, 4.99m, 5.60w, 5.87d,mw, 6.25mw, 6.76d,w, 7.06vw, 7.22w, 7.46mw, 7.64w, 8.04mw, 8.52w, 8.43w, 8.83vw, 9.13vw, 9.30w, 9.44w, 9.62w, 9.88vw, 10.07vw, 10.39w, 10.80vw, 11.25vvw, 11.62w, 11.90w, 12.22vw, 13.07w.

$TaF_5 \cdot Me_2SO$, I.R.; 3030mw, 1426w, 1418w, 1329mw, 1302w, 1043mw, 994m, 963b,vs, 922w, 905w, 720mw, 674s, 658w, 610b,sh, 582b,vs,asy, 470ms, 355m, 330b,sh, 240, s.

Raman; 673(15) some fluorescance.

$TaF_5 \cdot (Me_2SO\text{-}d_6)_2$, I.R.; 2268m, 2258sh, 2136mw, 1044w, 1027ms, 990sh, 974s, 943s, 839m, 829m, (794, 789)w, 770m, 642w, 580s,b, 570sh, 552s, 447mw, 430sh, 369w, 334mw, 310s, 255sh, 240, m.

Raman; 1031(21), 1016sh, 984(4), 947(9), (838, 829)(5), 785(w), 770(8), 689(30), 633(60), 602(55), 440b,w, 375b,w.

X-ray; 2.80vvs, 3.11vvs, 3.51vw, 3.63s, 4.27vw, 4.65s, 4.85vw, 5.02ms, 5.61vw, 5.89d,m, 6.27w, 6.42vvw, 6.74d,vw, 7.51d,w, 8.08w, 8.54vw, 8.67vw, 8.84vvw, 9.12vw, 9.31w, 9.46w, 9.64w.

$TaF_5 \cdot Me_2SO\text{-}d_6$, I.R.; 2285m, 2278m, 2145mw, 1046mw, 1027sh, 1020ms, 990sh,w, 957s,b, 910sh,b, 838m, 801w, 773m, (681, 676)s, 638sh, 586vs,asy,b, 441m, 337m, 325vw, 240, m,b.

Raman; 672(10), 638(10), some fluorescance.

X-ray; 3.00ms, 3.15vs, 3.58w, 3.89s, 4.25vs, 4.45ms, 4.93s, 5.65vw, 5.82vw, 5.98d,w, 6.37d,mw, 6.68w, 6.97w, 7.17w, 7.63vw, 7.79vvw, 7.92w, 8.18vw, 8.51w, 8.80vvw, 9.41w, 9.67w, 10.07w, 10.31w, 10.49vw, 10.77w, 11.03vw, 11.44vw, 11.55vw, 11.89vw, 12.56vw, 13.13vvw, 13.36w.

$NbF_5 \cdot (Me_2SO)_2$, I.R.; 3018w, 2325w, 2245vw, 2230vw, 1865w, 1432ms, 1418mw, (1331, 1324)mw, (1311, 1305)w, 1041mw, 1025mw, 1000sh, 993s,b, 966s, 935b,s, 722ms, 635sh, 610sh, 603b,s, 579m, 555m, 468ms, 452w, 380w, 358m, 380m, 265sh, 240, w.

X-ray; 2.95vs, 3.15_5vs, 3.46_5mw, 3.87vs, 4.32_5vs, 4.44_5s, 4.92vs, 5.64w, 5.98m, 6.24ms, 6.67_5m, 6.69m, 7.15m, 7.58_5w, 7.87_5w, 8.15mw, 8.48_5m, 8.65_5w, 9.00_5w, 9.40_5mw, 9.62mw, 9.80vw, 10.04_5mw, 10.26_5mw, 10.80w,d, 11.04_5w, 11.23w, 11.58w, 11.86_5w, 12.54_5w, 13.27mw.

$NbF_5 \cdot Me_2SO$, I.R.; 3030m, 1425w, 1418vw, 1325w, 1300vw, 1044m, 994m, 955s, 922w, 900w, 721mw, 664ms, 625vvs, 605b,vs,asy, 460s, 358m, 330w, 280sh,b, 250, s.

Raman; 665(15), some fluorescence.

X-ray; 2.23_5vvw, 2.93_5s, 3.14s, 3.55mw, 3.87_5s, 4.22vs, 4.43_5m, 4.93m, 5.95_5w, 6.35d,w, 6.65_5vw, 6.97vw, 7.18vvw, 7.61vvw, 7.89_5vw, 8.15_5vw, 8.50d,w, 8.82_5ww, 9.00_5vvw, 9.38vvw, 9.63vw, 10.08w, 10.28w, 10.51_5vvw, 10.78_5vw, 11.62_5vw, 13.28w.

"$TaF_5 \cdot Me_2SO \cdot Py$", I.R.; 1612s, 1491w, 1329w, 1244w, 1224m, 1160mw, 1071m, 1048m, (1040, 1036)w, 1019mw, 1006w, 995s, 953m, 922vs, 908m, 773w, 764m, 724m, 697s, 682w, 641m, 580vvs,b, 555sh, 497w, 482w,asy, 458w, 449w.

Raman; 693(13), some fluorescence.

X-ray; 2.66s,d, 3.05vvs,d, 3.30vw, 3.50vw, 3.53w, 3.79vw, 3.92vw, 4.17m, 4.28m, 4.58mw, 4.76w, 4.94w, 5.09vw, 5.26ms, 5.58d,w, 5.98w, 6.22w, 6.43vw, 6.81mw, 7.29w, 7.91w, 8.13vw, 8.51w, 8.78vw, 9.00vw,d.

$TaF_5 \cdot 2Py$, I.R.; 3290w,b, 3100m,b, 1930w, 1848w, 1609s, 1490m, 1230w, 1220w, 1159m, 1070s, 1045m, (1015, 1017)s, 950w, 870w, 760s, 690s, 651mw, 635m, 585b,vs, 448m, 330m.

Raman; 1611(10), 1575(10), 1227(10), 1048(55), 1019(150), 693(40), 644(45), 663(60), ~460(w), ~390(w), ~320(w), ~280(m), ~240(w), ~220(m), ~190(w), ~180(w), ~145(w). (Peaks below 460 cm^{-1} were found by Dr. D. Adams on a Codberg machine at Leicester University.)

$TaF_5 \cdot (Py\text{-}d_5)_2$, I.R.; 2476w, 2320w, 2300w, 2270vw, 1653w, 1593w, 1572s, 1539mw, 1329s, 1237w, 1049vw, 1025vw, 1014w, 982ms, 903m, 900sh, 850sh, (841, 835)m, 770w, 680w, 620sh, 610m, 590vs,b, 570sh, 532m, 410w, 328ms, 245sh.

Raman; 1569(20), 1537(50), 1347(20), 983(200), 902(70), 839(60), 780(10), 688.5(60), 625(90), 595(50),

424(w), 365(w), ~280(m), ~230(w), ~160(w), (peaks below 280 cm^{-1} were found by Dr. Adams).

X-ray; 1.58vw, 2.00vw, 2.58s, 2.67w, 2.87vw, 2.95s, 3.17w, 3.40s, 3.50_5mw, 3.81_5w, 3.98_5vw, 4.18vw, 4.39m, 4.51m, 4.84m, 5.01_5m, 5.24vw, 5.34w, 5.45vvw, 5.56vw, 5.75w, 5.89w, 6.12mw, 6.43_5w, 6.55vvw, 8.25w, 8.88w, 9.56m, 9.73mw, 9.88m, 10.23w, 10.43vw, 10.68vw, 11.10mw, 11.92w.

$NbF_5 \cdot 2Py$, I.R.; 1930w, 1850w, 1609m, 1490m, 1230m, 1221w, 1160m, 1071m, 1044m, (1019, 1015)m, 950w, 870w, 762ms, 692ms, 652w, 635w, 614b,s,asy, 602b,s, 584w, 563b,s, 453sh, 447m, 343m, 290b,sh, 240, m.

Raman; 1608(14), 1576(18), 1495(8), 1227(20), 1160(7), 1044(150), 1017(200), 676(55), 640(55), 587(100), 562(3), 414(5), 363(10).

X-ray; 1.57w, 1.99_5vw, 2.58s, 2.93vs, 3.16w, 3.39_5s, 3.53m, 3.84_5w, 4.08w, 4.21_5vvw, 4.39_5ms, 4.52_5ms, 4.84_5m, 5.00_5mw, 5.22_5vw, 5.54_5vw, 5.77vw, 5.90vw, 6.15w, 6.42_5vw, 6.58vw, 6.72_5vw, 6.94_5vw, 7.26w, 7.40w, 7.62w, 7.77_5vw, 7.97vw, 8.15_5vw, 8.22_5vw, 8.50vw, 8.67vw, 8.90_5vw, 9.18w, 9.57m, 9.84m.

$NbF_5 \cdot 2(Py\text{-}d_5)_2$, I.R.; 2650w,vb, 2475w, 2294w, 1650vw, 1566s, 1537w, 1336w, 1320vs, 1235w, 1165w, 1048w, 1024w, 1009w, 979s, 900m, (845, 838)m, 810w, 679m, 644sh, 610vs, 565s, 529s, 407m, 345m, 240, m.

Raman; 990(200), 906(50), 846(30), 788(15), 693(50), 632(100), 600(30).

$TaF_5 \cdot (4Me\text{-}Py)_2$, i.R.; 3100w, 2495w, 1954w, 1848w, 1780vw, 1678w, 1628s,asy, 1563w, 1511mw,asy, 1340w, 1243ms, 1218m, 1114w, 1070s, 1031s, (1012, 1008)w, 970w, 885w,b, 868w, 817s, 802vw, 724m, 704w, 656w, (584, 578)vs, 550mw, 506s, 332ms, 298w, 240, m.

Raman; 1629(10), 1070(20), 1034(40), 882(80), 688(40), 670(50), 613(90), 547(10), ~370(4), ~350(5), ~300(8), ~285(5), ~260(8), ~140(15). (Peaks below 400 cm^{-1} were found by Dr. Adams.)

X-ray; 1.69vw, 2.14_5vw, 2.46vvs,d, 2.75m, 3.20vw, 3.69vvs,d, 4.17w, 4.40s, 4.22vvw, 4.98mw, 5.22m, 5.65m, 5.87w, 6.11w, 6.45w, 6.69vw, 7.08vw, 7.48w, 7.67vvw, 8.01w, 8.47vw, 8.67vw, 8.90d,m, 9.43mw, 9.62w, 9.91vw, 10.05vvw, 10.36vvw, 10.50vvw, 1067vw, 11.51vw, 11.80w, 12.56w.

"$NbF_5 \cdot (4Me\text{-}Py)_2$", I.R.; 2726w, 2495w, 1945b,mw, 1845b,w, 1675s, 1585w, 1509w, 1339w, 1240m, 1214m, 1132w, 1114w, 1069s, 1040m, 1029m, 1008w, 970w, 888vw, 868mw, 819s, 795w, 724m, 703w, (693, 689)m, 654s, ~605vs,b, 568m, 555w,sh, 545w,sh, 503ms, 496w, 346s, 240, s.

Raman; ~686(4), ~665(5), 610(10), 600(4), (375, 362)(4).

$TaF_5 \cdot 2Me\text{-}Py$, I.R.; 3300b,mw, 3205b,w, (3100, 3090)w, 2030w, 1945w, 1900vw, 1860w, 1655w, 1639w, 1619s, 1582w,

1570m, 1561w, 1543w, 1499s, 1397w, 1319ms, 1233w, 1174ms, 1118m, 1073ms, 1035w, 1029s, 998w, 890w, 873m,b, (802, 798)mw, 772s, 720ms, 698s, 650m, 609vb,vs, 590sh,s, 554w, 468m, 430m, 415m, 318m,b, 220vs,b.

"$TaF_5 \cdot Me_2S$", I.R.; 1431vs, 1336m, 1316m*, 1039ms, 988ms, 920w, 840m*,b, 721w*, 705w, 660b,s, 630s, 570b,vs, 487m*,b.

(* Indicates band shapes varied from sample to sample.)

Raman; 745(14), 722(22), 690(25), 608(45).

"$NbF_5 \cdot Me_2S$", I.R.; 2930s, 1428s, 1332m, 1315mw*, 1039s, 984s, 924w, 718sh, 712s*, 670sh, 663vs, 638s*, 602vs*, 566vs, 475s,b, 328ms, 295m*,b, 240, s.

(* Indicates band shapes varied from sample to sample.)

Raman; 1439(10), 1421(3), 1335(6), 1050(3), 985(3), 742(15), 715(30), 686(25), 630(40), 582(100), 290(w).

"$NbF_5Me_2S + Me_2S$", slush, Raman; 580(35), 682(2), 691(7), 746(4).

"$NbCl_5 \cdot Me_2S$", I.R.; 1426s, 1328m, 1032ms, 982s, 793vs, 787sh, (735, 722)mw,b, 677mw, 372vvs.

"$NbF_5 \cdot Et_2S$", I.R.; 2980s, 2945ms, 2870m, 1453s,asy, 1428m, 1383ms, 1284m, 1266ms, 1079m, 1052m, 973s, 780m, 745w, 719w, 700s*, 655sh, 610-640vvs, 498b,s, 390m, 328w, 285s,sh, 250, s.

"$NbF_5 \cdot Et_2S$", I.R.; 2976vs, 2940m, 2878m, 1455w, 1426m, 1382ms, 1284m, 1262s, 1078m, 1050m, 975s, 898vw, 785m, 765w, 690vs,b, 650vvs,b, 585m, 510b,m, 473b,m, 305b,ms, 260b,m.

Raman; 1064(10), 976(3), 712(3), 682(10), 628(80), 592(26), 392(4),b, 335(2), (308, 289)(3), 246(3), (190, 182)(7), 136(10).

"$NbF_5 \cdot 2Et_2S$", Raman; 715(2), 691(2), 662(1), 641(1) 589(25).

Et_2S, 25°C, as a liquid film or in solution in CS_2, and CCl_4, I.R.; 2970vs, 2925s,asy, 2872m, 2854w, 2832w, 2804w, 2726w, 2690vvw, 2415w, 2225w, 1545b,m, 1520w, 1446vs,asy, 1427mw, 1374vs,asy, 1313w, 1252s,asy, 1072ms, 1045mw, 1035vw, 1000sh, 970ms, 780m, 760w, 734w, 696mw, 652mw, 637mw.

Et_2S, -196°C, not annealed; 2970-2860vvs,b, 2725m, 2700sh, 2490b,w, 2446w, 2350ms, 2226mw, 2160w, 1513m, 1440vvs,vb, 1373vs, (1322, 1314)mw, 1280sh, 1255vs,b, 1076s, 1047ms, 1030sh, 1015vvw, 1008mw, 970vs,asy, 893w, 795vs,b, 773s, 738s, 692s, 654s, 636s.

Et_2S, -196°C, annealed, or solutions of Et_2S in CS_2, or CCl_2 cooled to -196°C, I.R.; 2920vs,b, 2870vs, 2740ms, 273m, 2352m, 2276w, 2240m, 1945mw, 1510w, 1490vw, 1439vs,asy, 1373vs,asy, 1323mw, 1279vs, 1250vs, 1079s, 1041s, 1035sh,w,

1025sh,w, 990m, 983vs, 795vs, 762w, 735w, 688vs, 660ms, 650mw.

$TaF_5 \cdot 2NHMe_2$, I.R.; 3282s, 3020w, 1412w, 1404w, 1284ms, 1223m, 1122m, 1084m, 1063ms, 1022s, 901s, 721m, 639ms, 568vvs,b,asy, 534vs,b, (465, 458)w, 340s, 314w, 276m.

Raman; 1470(20), 1280(7), 1220(5), 1059(10), 1026(10), 905(15), 640(100).

"$NbF_5 \cdot NHMe_2$", I.R.; 3316s,b, 3140b,sh, 2450w, 1610mw,b, 1300b,w, 1258w, 1214w, (1130, 1122)mw, 1045m,asy, 1020ms, 958m, 908m, 854mw,b, 720mw, 609s,asy,b, 592mw, 551m, 482m.

Raman; 958(15), 892(3), 678(7), 587(w), 560(3), 356(5).

"$TaF_5 \cdot 2NHEt_2$", I.R.; 3215b,s, 3148m,sh, 2945ms, 2468mw, 1588b,ms, 1392w, 1360m, 1342vw, 1328vw, 1306mw, 1280w, 1192s, 1158m, 1129m, 1094ms, 1049s,b,asy, 1008s, 965w, 910ms, 845w, 790s,b,asy, 778s, 722mw, 693mw, 645m, 580vs,b, 545vs,b, 450b,ms, 380b,m, 350w, 280m,b, 240, s.

$TaF_4 \cdot NEt_2$, I.R.; 1364w, 1339w, 1330w, 1276w, 1192ms, 1126m, 1093ms, 1071m, 1043ms, 1004s, 917ms, 905w, 794ms, 723mw, 666s, 638vs, 620vs, 550w, 499s,b, 420w, 365m,b, 306m, 240, s.

Raman; 1003(15), 919(20), 662(28), 598(18), 305(10).

X-ray, 2.04d, vvs, 2.28vw, 2.49s, 2.96vw, 3.24s, 3.46vs, 3.55vvw, 3.64vw, 3.85ms, 4.10mw, 4.43_5m, 4.64vw,

7.85mw, 8.36mw, 8.75mw, 9.05w, 9.39d,w, 9.70w, 9.86m, 10.23vvw, 10.57vvw, 10.87vw, 11.16vw, 11.53vw, 11.90vvw, 12.12w.

$NbF_3 \cdot (NEt_2)_2$, I.R.; 2660w, 1351mw, 1338w,sh, 1320w,sh, 1278m, 1190ms, 1136s, 1090ms, 1068ms, 1050ms, 1000vs;asy, 906sh,w, 890vs, 843w, 790s, 723w, 630vs, 610w, 584vs, 458vs,b, 330sh, 320ms, 306sh.

Raman; 1013(6), 900(12), 800vw, 593(10), 490(vw), 445(vw), 345(5).

X-ray; 1.53vvs, 1.97vvs, 2.42vvw, 2.70m, 2.99s, 3.13m, 3.35_5vw, 3.58_5w, 3.79_5mw, 4.13w, 4.36mw, 4.73w, 4.91ms, 5.10_5vw, 5.40w, 5.57mw, 5.87m, 6.12vw, 6.38vw, 6.81d,m, 7.74vvw, 7.99vvw, 8.38vw, 8.60vw, 8.77vw, 9.09vw, 9.58m, 9.86w.

$TaF_4 \cdot NEt_2 \cdot Py$, I.R.; 2485w, 1990w,b, 1870vw, 1840vw, 1650b,w, 1612s, 1576vw, 1450vs, 1366w, 1358w, 1278w, 1243w, 1230vw, 1219m, 1193m, 1159w, 1130m, 1095mw, 1069s, 1049s, 1008s,b,asy, 956w, 906s,asy, 792m, 762s, 697s, 681w, 644s, 631w, 590vs, 580vvs, 450w, 433w, 336m, 310m,b, 262m, 240, s.

Raman; 648(12), 632(13), 581(7), 316(5) (some fluorescence).

X-ray; 2.56vs, 3.05ms, 3.28ms, 3.35_5ms, 3.56vvw, 3.78vvw, 4.26s, 4.55_5mw, 4.88m, 5.33mw, 5.46w, 5.85m, 6.13mw, 6.63mw, 7.30mw, 7.42vvw, 7.595w, 8.01w, 8.32vw, 8.57vw,

4.82m, 5.05d,m, 5.29d,vs, 5.52w, 5.78vw, 5.97_5vw, 6.07vw, 6.22_5vw, 6.43w, 6.87w, 7.05w, 7.30mw, 7.52w, 7.86mw, 8.30vvw, 8.70_5w, 9.03vw, 9.22vw, 9.38vw, 9.43vw, 9.84m, 9.96vvw, 10.20vvw, 10.29vw, 10.54vw, 10.81w, 11.15vw, 11.36vw, 11.54w, 11.85vw, 12.08w.

$TaF_3 \cdot (NEt_2)_2$, I.R.; 2656b,w, 1356w, 1335mw, 1278m, 1191s, (1142, 1136)s, 1094s, 1066w, 1052ms, 1018m, 1002s, 904w, 894s, 789s, 723m, 662w, 610vs,b,asy, 595sh, 523mw, 475vs,b, 292ms,b,asy.

X-ray; 1.43w, 2.05vs, 2.63s, 3.04m, 3.44w, 4.21_5mw, 4.27mw, 4.41m, 4.88_5w, 4.97_5ms, 5.09_5vvw, 5.31vw, 5.52w, 5.68mw, 5.93mw, 6.14_5vvw, 6.36vw, 6.84m, 7.01vvw, 7.24vvw, 7.37vw, 7.53vvw, 7.85vvw, 7.95vvw, 8.07vvw, 8.22vw, 8.55vw, 8.75vvw, 8.81_5vvw, 8.98vvw, 9.03vw, 9.55_5vvw, 9.68m, 9.75m, 9.94w, 10.00w, 10.21vw, 10.29vw, 11.02d,m.

$NbF_4 \cdot NEt_2$, I.R.; 1590w,b, 1368vw, 1351w, 1338vw, 1324w, 1272mw, 1189m, 1124s, 1092ms, 1069ms, 1035ms, 994s, 907sh, 901s,asy, 793ms, 722w, 674w, 646vs,asy,b, 622w, 600vs, 595w, 480s,b, 325ms.

Raman; 1454(10), 1380(6), 1187(15), 1071(7), 1033(7), 994(30), 898(40), 790(8), 638(15), 594(28), 334(25).

X-ray; 2.05(vs), 2.31vw, 2.49m, 2.73vw, 3.26m, 3.43s, 3.53vvvw, 3.69vvw, 3.87m, 4.13mw, 4.45mw, 4.62_5vvw, 4.82_5vvw, 5.01m, 5.09m, 5.29s, 5.37mw, 5.55mw, 5.78_5mw, 5.91mw, 6.09w, 6.27vw, 6.49w, 6.91w, 7.10w, 7.34mw, 7.65w,

8.79vw, 8.97vw, 9.06vvw, 9.40vvw, 9.48vw, 9.65vw, 9.91w, 10.13vw, 10.36w, 10.75w, 11.88vw.

$TaF_3 \cdot (NEt_2)_2Py$, I.R.; 3090w, 2000w, 1941w, 1890vw, 1870vw, 1720vw, 1652w,b, 1611s, 1576w, 1491w, 1354w, 1336w, 1322w, 1281mw, 1240w, 1224m, 1192s, 1162mw, 1135s, (1095, 1088)ms, 1067s, 1048s, 1004vs,asy, 904w, 893s, 820w, 794w, 788s, 770s, 722mw, 707w, 199s, 680w, 654w, 640s, 565vs, 539w, 519vs, 437m, 311m, 250mw,sh, 240, m.

Raman; strong fluorescence.

X-ray; 1.47w, 2.41vs, 3.02s, 3.63mw, 3.79mw, 4.10vvw, 4.32vvw, 4.51w, 4.90_5w, 5.05vw, 5.94mw, 6.19vw, 6.58vw, 8.10vw.

$NbF_3 \cdot (NEt_2)_2Py$, I.R.; 3080w, (2665, 2640)w, 1605s, 1348m, 1331w, 1317w, 1276mw, 1240w, 1220m, 1186m, 1156w, 1132m, 1086m,asy, 1061ms,asy, 1044m, 998s,asy, 902w, 889sh, 883s, 792sh, 786m, 766ms, 698ms, 653mw, 636m, 590sh, 576vs,b, 557sh, 542sh, 511s, 435w, 340sh, 326ms, 303sh,w.

$NbF_3 \cdot NEt_2 + NbF_5 \cdot OEt_2 + Et_2O$, X-ray; 1.48vw, 1.73mw, 2.00mw, 2.23vs, 2.46vs, 2.69vw, 2.85vvw, 3.05vw, 3.32mw, 3.58_5w, 3.84vvw, 4.50w, 4.69w, 5.07w, 5.24vw, 5.78vw, 9.61m, 9.83w, 9.15mw.

$TaF_4 \cdot NEt_2 \cdot 4Me\text{-}Py$, I.R.; 2760b,w, 2496w, 2180b,w, 2090b,w, 1950w, 1844w, 1780vw, 1686w, 1624s, 1565w,b, (1511, 1508)mw, 1350w, 1240m, 1233vw, 1215m, 1210w, 1195mw,

1129m, 1045mw, 1069s, 1052w, 1030s, 1007m, 907ms, 815s, 789mw, 724m, 704w, 667w, 635m, 583vs,b,asy, 548w, 505m, 497w, 334m, 298m, 240, m.

X-ray; 2.47vvs,d, 2.75m, 3.10s, 3.33ms, 3.70s, 4.21s, 4.39ms, 4.59ms, 4.76vw, 5.06m, 5.22w, 5.41m, 5.72m, 5.96vw, 6.13m, 6.30w, 6.52w, 6.72vw, 6.92vw, 7.15m, 7.29mw, 7.49m, 7.97m, 8.28mw, 8.37mw, 8.61w, 8.81w, 8.94_5w, 9.16w, 9.45vw, 9.87w, 10.29w, 10.86w, 11.81mw.

$TaF_3 \cdot (NEt_2)_2 \cdot$4Me-Py, I.R.; 3755vvw, 3720vw, 3136w, 3075mw, 3045mw, 2965vvs, 2926vs, 2860vs, 2720vw, 2680w, 2550vw, 2480mw, 2410vw, 2260vw, 2230w, 2140vw, 2032w, 1945mw,b, 1850w,b, 1770w,b, 1680w,b, 1628s,asy, 1558mw, 1505w, 1462w, 1446s, 1425w, 1373s, 1354m, 1335sh, 1320w, 1280mw, 1233m, 1219vw, 1212m, 1189vs, 1134s, 1094s, 1070m, 1050vs, 1008vs,asy, 889vs,asy, 814s, 791s, 725m, 705mw, 671w, 654m, 643m, 565vvs,b, 497ms, 303m, 250, s.

$NbCl_{0.5}F_{4.5}$2Py, I.R.; 3124w, 2486w, 1985w, 1933w, 1851w, 1710w, 1655w, 1611s, 1580w, 1491m, 1451vs, 1243w, 1228w, 1222m, 1163m, 1071s, 1045m, 1019s, 953w, 762s, 694s, 663mw, 637s, 620sh, 611vs,b, 600w, 570ms, 458mw, 450mw, 345vs, 325sh, 240, ms.

Raman; 1608(12), 1576(12), 1493(5), 1227(22), 1161(7), 1043(65), 1017(100), 695(2), 675(10), 662(7), 651sh, 641(50), 612(2), 586(85), 567(3), 349(4), 311(4).

X-ray; 1.75w, 2.24vw, 2.62vs, 2.76_5s, 2.96w, 3.13_5vs,

3.31_5w, 3.59_5s, 3.85_5w, 4.10_5w, 4.52_5s, 4.72_5s, 4.91_5vvw, 5.04w, 5.14vw, 5.51m, 6.19vvw, 6.31_5w, 6.67w, 6.79w, 6.93w, 7.20vw, 7.43mw, 7.56_5vw, 7.76_5vvw, 8.10w, 8.52_5vw, 8.58vw, 8.92w,d, 9.15vw, 9.28vvw, 9.40w, 9.64_5vw, 10.66w.

$NbClF_4 \cdot 2Py$, I.R.; 2484w, 1995vw, 1980vw, 1932w, 1849w, 1650w, 1614s, 1580w, 1491mw, 1450vs, 1243mw, 1228m, 1221ms, 1162m, 1971s, 1044m, 1018s, 973w, 933w, 762s, 722w, 694vs, 665mw, 656w, 652ms, 636s, 625m, 610vs, 600mw, 572s, 458w, 450mw, 342vs, 240, m.

Raman; 1608(8), 1575(7), 1493(2), 1227(10), 1043(60), 1016(90), 681(vw), 663(8), 651(7), 642(50), 611(4), 587(70), 567(3), 371(9), 343(7), 314(w), 267(vw).

X-ray; 1.24_5vw, 2.27vvw, 2.59_5vs, 2.76ms, 3.09_5vs, 3.29_5vw, 3.56_5d,m, 3.81vvw, 4.06_5vw, 4.49ms, 4.76w, 5.40_5w, 5.51w, 6.27w, 6.62w, 6.85_5vw, 7.33_5d, 7.92_5w, 8.86w, 9.11vw, 9.30_5vw, 9.57w.

$NbCl_2F_3 \cdot 2Py$, I.R.; 2480w, 1994w, 1980w, 1930mw, 1850w, 1610s, 1576w, 1490w, 1448vs, 1242m, 1226sh, 1221s, 1161s, 1040s, 1043m, 1016s, 975w, 950w, 944w, 870w, 762s, 693vs, 657mw, 653mw, 634vs, 610vs, 600m, 570s, 458mw, 450m, 240, m.

Raman; 1607(10), 1575(8), 1443(3), 1227(10), 1044(65), 1018(95), 893(4), 650(sh), 641(50), 633(sh), 610(30), 588(80), 369(30), ~350b,(10).

X-ray; 1.67_5vw, 2.29mw, 2.56_5vs, 2.73_5ms, 3.03_5vs, 3.24vw, 3.42_5w, 3.55_5vw, 3.72vw, 4.02vw, 4.38_5m, 4.49w, 4.65m, 4.93w, 5.28_5vw, 6.13w, 6.25vvw, 6.53_5d,w, 6.76_5vvw, 7.00vvw, 7.33w, 7.45vvw, 7.81_5w, 8.04vvw, 8.22_5vvw, 8.47_5vvw, 8.64vw, 8.96_5vw, 9.15vw, 9.68vw, 9.91vw, 11.14d,w.

$NbCl_3F_2 \cdot 2Py$, I.R.; 1935w, 1884w, 1608s, 1490w, 1447s, 1238mw, 1223ms, 1158mw, 1070s, 1043m, 1014s, 945w, 870s, 760s, 693s, 655mw, 637ms, 632ms, 607s, 585w, 574mw, 450mw, 435vw, 422vw, 410mw, 360sh, 335vs,b.

Raman; 1044(14), 1017(18), 640(7), 594(6), 424(15), 368(45).

X-ray; 1.62vw, 2.29w, 2.51s, 2.72m, 2.98s, 3.22_5w, 3.40mw, 3.52vw, 3.71w, 3.97vw, 4.33ms, 4.63mw, 4.92w, 5.23vw, 5.39vvw, 5.81_5w, 6.52mw, 7.10w, 7.41vvw, 7.69vw, 8.00vw, 8.67_5vvw, 8.85_5vvw, 9.11w, 9.44w, 10.18vw, 10.82vw.

"$NbCl_4F \cdot 2Py$", I.R.; 1922vw, 1840vw, 1608ms, 1487sh, 1446s, 1238w, 1225m, 1158mw, 1071ms, 1043mw, 1013ms, 970w, 950w, 760ms, 723w, 691s, 654mw, 636ms, 608s, 585sh, 567sh, 450mw, 434mw, 422vw, 355sh, 335vs,b.

Raman; 1050(8), 1018(20), 593(5), 423(20), 366(35).

X-ray; 1.65m, 2.28_5s, 2.51s, 2.70_5m, 3.01_5d,vs, 3.22_5s, 3.37_5w, 3.52_5w, 3.72w, 4.32s,d, 4.62mw, 4.92w, 5.33vw, 5.81m, 6.08vvw, 6.17_5vvw, 6.49mw, 6.86vw, 7.12w, 7.40_5vw, 7.81_5vw, 7.95w, 8.35vw, 8.82vw, 9.14vw, 9.39_5vw,

9.66_5w, 9.88_5w, 10.17w, 11.27vw.

$NbCl_5 \cdot Py$, I.R.; 2000vw, 1924vw, 1651vw, 1610s, 1599sh,w, 1496w, 1449vs, 1306vw, 1255w, 1229ms, 1159mw, 1086w, 1071s, 1044s, 1013s, 980w, 849w, 757s, 691vs, 677w, 636ms, 437m, 420w,sh, 409s, 385sh, 352vs,b, 286sh.

Raman; 1605(6), 1227(s), 1044(8), 1012(40), 420(40), 361(7?-.

X-ray; 2.83_5vw, 3.04_5d,vs, 3.40w, 3.58_5vvw, 3.82_5w, 4.36_5d,mw, 4.65w, 5.02d,w, 5.67_5vvw, 5.84_5s, 6.16_5vw, 6.71_5vw, 6.86_5vw, 7.18_5w, 7.76vw, 7.95_5mw, 8.29w, 8.84w, 9.30d,w, 9.86w, 10.24w.

$NbCl_5 \cdot OEt_2$, I.R.; 1315w,asy, 1273w, 1184mw, 1179sh, 1142mw, 1084m, 1015sh, 984vs,asy, 871s, 823mw, 755s, 505m, 459w, 388m, 370vvs, 355vs, 320w,sh, 280sh.

Raman; 1474(4), 1415(12), 1382(3), 1366(8), 1316(7), 1081(12), 985(4), 754(4), 505(2), 384(130), 356(50), 298(13), 161(20).

X-ray; 2.48m, 2.82mw, 3.03ms, 3.12ms, 3.26ms, 3.80m, 4.11vw, 4.26w, 4.83w, 5.10vw, 5.41w, 5.73w, 5.79w, 6.04vw, 6.24mw, 6.55mw, 6.80w, 7.03w, 7.45vw, 7.70vw, 7.85vw, 8.12mw, 8.70d,w, 9.00w, 9.45w, 9.41w, 10.72w.

Mass Spectra:

Appearance potentials (A.P.) are not corrected for the machine work-function.

$NbF_5 \cdot OEt_2$ at 25°C and 70°C; 169s (NbF_4^+), 166ms

($NbOF_3^+$?), 150s (NbF_3^+), 147m ($NbOF_2^+$), 131s (NbF_2^+), 112s (NbF^+), 935 (Nb^+) + many peaks attributable to organic fragments.

$NbF_5 \cdot OMe$ at 25°C, 169s (NbF_4^+), 150s (NbF_3^+) 131s (NbF_2^+), 112s (NbF^+), 93s (Nb^+).

TaF_5 at 70°C, 257s (TaF_4^+), A.P. = 18.5 ev, 238s (TaF_3^++, A.P. = 24 ev, 219s (TaF_2^+), A.P. = 34 ev, 200s (TaF^+), A.P. = 40 ev, 181s (Ta^+), A.P. = 49 ev.

NbF_5 at 70°C, 169s, 150s, 131s, 112s, 93s, attributable to NbF_4^+, NbF_3^+, NbF_2^+, NbF^+, Nb^+ respectively.

Appendix IV

Ratios of energies of nuclear quadrupole transitions in the ^{93}Nb 9/2 spin system.

η^2	η	9/2–7/2	7/2–5/2	$\frac{9/2-7/2}{7/2-5/2}$	5/2–3/2	$\frac{7/2-5/2}{5/2-3/2}$
0	0	4·00000	3·00000	1·33̇	2·00000	1·5000
0·01	0·1	3·99676	2·99439	1·3347	1·97540	1·5158
0·02	0·1414	3·99352	2·98872	1·3362	1·95449	1·5292
0·03	0,1732	3·99027	2·98297	1·3377	1·93659	1·5403
0·04	0·20	3·9870	2·97717	1·3392	1·92119	1·5496
0·05	0·2236	3·98377	2·(µ131	1·3407	1·90792	1·5574
0·06	0·2449	3·98051	2·96540	1·3423	1·89650	1·5636
0·07	0·2646	3·97725	2·95946	1·3439	1·88670	1·5686
0·08	0·2828	3·97398	2·95344	1·3455	1·87833	1·5724
0·09	0·3	3·97071	2·94740	1·3472	1·87125	1·5751
0·10	0·3162	3·96744	2·94132	1·3489	1·86532	1·5768
0·11	0·3366	3·96417	2·93521	1·3506	1·86045	1·5777
0·12	0·3464	3·96089	2·92907	1·3523	1·85653	1·5777
0·16	0·4	3·94773	2·9043	1·3593	1·84897	
0·25	0·5	3·91789	2·84826	1·3755	1·86591	
0·36	0·6	3·88097	2·78128	1·3954	1·92515	
0·49	0·7	3·83665	2·70715		2·02395	1·3376
0·64	0·8	3·78457	2·63076		2·15624	1·2794
0·81	0·9	3·72430	2·55735		2·31464	1·1049
1·00	1·0	3·65545	2·49193	1·4669	2·49193	1·0000

3/2–1/2	$\frac{3/2-1/2}{5/2-3/2}$	$\frac{7/2-5/2}{3/2-1/2}$	$\frac{9/2-7/2}{3/2-1/2}$
1·00000	1/2		
1·08614	1/1·18187		
1·16500	1/1·6777		
1·23827	1/1·5639		
1·30663	1/1·4703		
1·37093	1/1·3917		
1·43170	1/1·3246		
1·48940	1/1·2611		
1·54437	1/1·2162		
1·59691	1/1·1718		
1·64726	1/1·13237		
1·69563	1/1·0972		
1·74219	1/1·0656		
1·91302	1·0346	1·51817	
2·23173	1·1961	1·2763	
2·54193	1·3204	1·0942	
2·83928		1/1·0488	1·3513
3·12316		1/1·1872	1·2118
3·33946		1/1·3274	1·0917
3·65545	1·4669	1/1·4669	1·0000

Appendix V

Suggestions for future work

1) Sb, and Ta both have nuclei with quadrupole moments and an analysis of e^2Qq and η for Nb, Sb, Ta nuclei in various bridging fluoride compounds (e.g. $NbF_5 \cdot SbF_5$, $MF_5 \cdot SeF_4$, $MF_5 \cdot (XeF_2)_x$) similar to that made for $NbF_5 \cdot XeF_2$ should yield interesting results.

2) Niobium and tantalum chloride-fluorides have been made here using ether as a solvent. Use of $AsCl_3$ as a solvent for the reactions

$$3NbCl_5 + AsF_3 \rightarrow AsCl_3 + 3NbCl_4F$$

$$3NbCl_4F + 4AsF_3 \rightarrow 4AsCl_3 + 3NbCl_5$$

has been reported in the literature. There is no obvious reason why $AsCl_3$ should not be used as a solvent for the reaction

$$NbF_5 + Me_3SiCl \rightarrow NbCl_xFy$$

The conductivity data of Kolditz (Z. Anorg. Chem. (1964), 312, 11) show possible inflections in the conductivity-composition curves for Nb fluoride-chlorides at the compositions $NbCl_2F_3$ and $NbClF_4$. By stoichiometric addition of Me_3SiCl to NbF_5 in $AsCl_3$, followed by removal of volatiles new chloride-fluorides might be obtained. The products should be analysed by X-ray powder photography,

and Raman and I.R. spectroscopy from 60 - 1050 cm^{-1}.

3) Reaction of NbF_5, or TaF_5 with Me_3SiNEt_2 in the ratio 1:x, (x = 1·25, 1·5, 1·75 etc.) in solution in Et_2O may yield new compounds. If these could be isolated they would be almost conclusive proof of polymerisation in M-F-NEt_2 compounds.

4) $NbCl_x(CN)_y$ compounds are known as products of the reaction of $NbCl_5$ with HCN. The reaction of HCN with NbF_5 may yield purer products than the reaction of Me_3SiCN and NbF_5. An unreported reaction of Me_3SiCN and SOF_4 (performed by J.C. Fuggle and D.S. Ross) yielded large colourless crystals which were slightly volatile. Reaction of Me_3SiCN with other fluorides (WF_6, MoF_6, PF_5, etc.) would be worth investigating because fluoride cyanides are possible precursors to lower fluorides, and a range of fluoride-alkyl compounds.

5) It was extremely difficult to remove $NHMe_2$ from the reactions of NbF_5, or TaF_5 and $NHMe_2$ (see section 1:7). This suggests that there may be weak compounds between the pentafluoride molecules and large numbers of $NHMe_2$ molecules. An investigation of the relationship between the ratio of MF_5:$NHMe_2$ and vapour pressures over the mixtures should yield information on the system.